

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C11D 3/39, 1/65, 17/00 // 1:62, 1:02	A1	(11) International Publication Number: WO 97/43390 (43) International Publication Date: 20 November 1997 (20.11.97)
(21) International Application Number: PCT/US97/08439		
(22) International Filing Date: 16 May 1997 (16.05.97)		
(30) Priority Data: 60/017,886 17 May 1996 (17.05.96) US		
(71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).		3JU (GB). HARTSHORN, Richard, Timothy [GB/GB]; 139 Dene Road, Wylam, Northumberland NE41 8EY (GB). MANOHAR, Sanjeev, Krishnadas [US/US]; 2014 B Meadowlawn Way, Fairfield, OH 45014 (US). KATSUDA, Rinko [JP/JP]; Kobe Park City C507, 6-2-1, Chuo-ku, Kobe 650 (JP). KVIETOK, Frank, Andrej [US/US]; 1103 Richwood Avenue, Cincinnati, OH 45208 (US). MAO, Mark, Hsiang-Kuen [US/JP]; 2-23-13, Honmachi, Sumiyoshi, Kobe 658 (JP). MOSS, Michael, Alan, John [GB/GB]; 13 Painshawfield Road, Stocksfield, Northumberland NE43 7DZ (GB). MURATA, Susumu [JP/JP]; 6-5-A3, Yuba-cho, Nishinomiya-City, Hyogo 662 (JP). FOLEY, Peter, Robert [GB/US]; Apartment 906, One Lytle Place, Cincinnati, OH 45202 (US). PANANDIKER, Rajan, Keshav [US/US]; 6484 Oregon Pass, West Chester, OH 45069 (US). PRAMOD, Kakumanu [IN/US]; 7986 Kingfisher Lane, West Chester, OH 45069 (US). SARNAIK, Khizar, Mohamed, Khan [IN/JP]; 5-1-523-302, Koyo-cho Naka, Kobe 658 (JP). THOEN, Christian, Arthur, Jacques, Kamiel [BE/BE]; Boekweithofstraat 4, B-9120 Haasdonk (BE).
(72) Inventors; and		
(75) Inventors/Applicants (for US only): ASANO, Kaori [JP/JP]; Ohgi 5-16-1-207, Higashinada-ku, Kobe, Hyogo (JP). SCHEIBEL, Jeffrey, John [US/US]; 10400 Buxton Lane, Montgomery, OH 45242-5306 (US). MINAMIKAWA, Kaori [JP/JP]; 1-26-46, Mitachi-higashi Himeji, Hyogo 670 (JP). CRON, Laura [US/US]; 5656 Lake Mead Drive, Fairfield, OH 45202 (US). KOTT, Kevin, Lee [US/US]; 2920 Bentbrook Drive, Cincinnati, OH 45251 (US). CRIPE, Thomas, Anthony [US/US]; 599 Three Chimneys Lane, Loveland, OH 45140 (US). CURRY, John, Downing [US/US]; 95 Stone Creek Drive, Oxford, OH 45056 (US). WILLMAN, Kenneth, William [US/US]; 5603 Williamsburg Way, Fairfield, OH 45014 (US). DODD, Ian, Martin [GB/GB]; 47 Holywell Drive, Loughborough LE11		
		(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).
		(81) Designated States: BR, CA, CN, CZ, HU, JP, MX, TR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DETERGENT COMPOSITION		
(57) Abstract		A detergent composition comprising an alkoxylated quaternary ammonium (AQA) cationic surfactant, a non-AQA surfactant and a percarbonate bleach.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KR	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

DETERGENT COMPOSITION

5

Technical Field

10 The present invention relates to a detergent composition comprising percarbonate bleach, an alkoxyolated quaternary ammonium (AQA) cationic surfactant and a non-AQA surfactant.

Background to the Invention

15 The formulation of laundry detergents and other cleaning compositions presents a considerable challenge, since modern compositions are required to remove a variety of soils and stains from diverse substrates. Thus, laundry detergents, hard surface cleaners, shampoos and other personal cleansing compositions, hand dishwashing detergents and detergent compositions suitable for use in automatic dishwashers, all require the proper selection and combination of ingredients in order to function effectively. In general, such detergent compositions will contain one or more types of surfactants which are designed to loosen and remove different types of soils and stains. While a review of the literature would seem to indicate that a wide selection of surfactants and surfactant combinations are available to the detergent manufacturer, the reality is that many such ingredients are speciality chemicals which are not suitable in low unit cost items such as home-use laundry detergents. The fact remains that most such home-use products such as laundry detergents still mainly comprise one or more of the conventional ethoxylated nonionic and/or sulfated or sulfonated anionic surfactants, presumably due to economic considerations and the need to formulate compositions which function reasonably well with a variety of soils and stains and a variety of fabrics.

30 The quick and efficient removal of different types of soils and stains such as body soils, greasy/oily soils and certain food stains, can be problematic. Such soils comprise a mixture of hydrophobic triglycerides, lipids, complex polysaccharides, inorganic salts and proteinaceous matter and are thus notoriously difficult to remove. Low levels of

2 PAGES

hydrophobic soils and residual stains often remain on the surface of the fabric after washing. Successive washing and wearing coupled with limited hydrophobic soil removal in the wash culminates in a build up of residual soil and stain which further entraps particulate dirt leading to fabric yellowing. Eventually the fabric takes on a
5 dingy appearance which is perceived as unwearable and discarded by the consumer.

The literature suggests that various nitrogen-containing cationic surfactants would be useful in a variety of cleaning compositions. Such materials, typically in the form of amino-, amido-, or quaternary ammonium or imidazolinium compounds, are often
10 designed for speciality use. For example, various amino and quaternary ammonium surfactants have been suggested for use in shampoo compositions and are said to provide cosmetic benefits to hair. Other nitrogen-containing surfactants are used in some laundry detergents to provide a fabric softening and anti-static benefit. For the most part, however, the commercial use of such materials has been limited by the
15 difficulty encountered in the large scale manufacture of such compounds. An additional limitation has been the potential precipitation of anionic active components of the detergent composition occasioned by their ionic interaction with cationic surfactants. The aforementioned nonionic and anionic surfactants remain the major surfactant components in today's laundry compositions.

20 It has now been discovered that certain alkoxylated quaternary ammonium (AQA) compounds can be used in various detergent compositions to boost detergency performance on a variety of soil and stain types, particularly the hydrophobic soil types, commonly encountered. Unexpectedly, it has now been discovered that compositions
25 containing AQA surfactants and percarbonate bleach deliver superior cleaning and whiteness performance versus products containing either technology alone.

The AQA surfactants of the present invention provide substantial benefits to the formulator, over cationic surfactants previously known. For example, the AQA
30 surfactants used herein provide marked improvement in cleaning of "everyday" greasy/oily hydrophobic soils regularly encountered. Moreover, the AQA surfactants are compatible with anionic surfactants commonly used in detergent compositions such as alkyl sulfate and alkyl benzene sulfonate; incompatibility with anionic components of the detergent composition has commonly been one of the limiting factor in the use of
35 cationic surfactants previously known. Low levels (as low as 3 ppm in the laundering liquor) of AQA surfactants gives rise to the benefits described herein. AQA surfactants

can be formulated over a broad pH range from 5 to 12. The AQA surfactants can be prepared as 30% (wt.) solutions which are pumpable, and therefore easy to handle in a manufacturing plant. AQA surfactants with degrees of ethoxylation above 5 are sometimes present in a liquid form and can therefore be provided as 100% neat

5 materials. In addition to their beneficial handling properties, the availability of AQA surfactants as highly concentrated solutions provides a substantial economic advantage in transportation costs. The AQA surfactants are also compatible with various perfume ingredients, unlike some cationic surfactants known in the art.

10 Percarbonate, which delivers peroxide bleach into the wash, is a cornerstone technology of modern, ultra-compact granular laundry detergent formulas. Peroxide bleach is hydrophilic and, while it cannot match the bleaching effectiveness delivered by peracids (formed for example from peroxide interaction with TAED), it is effective at decolouration of pigments (e.g. in particulate or beverage stains) and also can help

15 remove the colour from the organic residues associated with body soils.

It is believed that the greasy/oily soils are effectively solubilized by AQA, thereby allowing access of the hydrophilic peroxide bleach to the colour bodies in the soil (e.g. entrapped pigments) resulting in improved soil decolouration. The present invention thus provides a detergent composition which delivers superior cleaning in such much as the composition provides marked cleaning effectiveness against both hydrophobic greasy/oily and hydrophilic coloured soils.

BACKGROUND ART

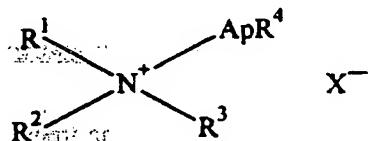
25

U.S. Patent 5,441,541, issued August 15, 1995, to A. Mehreteab and F. J. Loprest, relates to anionic/cationic surfactant mixtures. U.K. 2,040,990, issued 3 Sept., 1980, to A. P. Murphy, R.J.M. Smith and M. P. Brooks, relates to ethoxylated cationics in laundry detergents.

30

Summary of the Invention

The present invention provides a composition comprising or prepared by combining a percarbonate bleach a non-AQA surfactant and an effective amount of an alkoxylated quaternary ammonium (AQA) cationic surfactant of the formula:



wherein R¹ is a linear, branched or substituted C₈-C₁₈ alkyl, alkenyl, aryl, alkaryl, ether or glycidyl ether moiety, R² is a C₁-C₃ alkyl moiety, R³ and R⁴ can vary independently and are selected from hydrogen, methyl and ethyl, X is an anion, A is C₁-C₄ alkoxy and p is an integer in the range of from 2 to 30.

Detailed Description of the InventionPercarbonate Bleach

The first essential component of the present invention is a percarbonate bleach. Alkali metal or alkali earth metal percarbonates, particularly sodium percarbonate are preferred percarbonates for inclusion in compositions in accordance with this invention.

Sodium percarbonate is an addition compound having a formula corresponding to 20 2Na₂CO₃.3H₂O₂, and is available commercially as a crystalline solid. Commercial suppliers include Solvay, FMC, Tokai Denka and others.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from 0.5 mm to 1 mm, not more than 10% by weight of said particles being smaller than 0.2 mm and not more than 10% by weight of said particles being larger than 1.250 mm.

Percarbonate can be present at levels of between 1% and 50%, preferably between 1% and 30%, most preferably between 5% and 20% by weight of detergent composition. 30 The percarbonate is most preferably incorporated into such compositions in a coated form which provides in-product stability.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interrox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in 5 the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $\text{Na}_2\text{SO}_4 \cdot n \cdot \text{Na}_2\text{CO}_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

10 Other coatings which contain silicate (alone or with borate salts or boric acids or other inorganics), waxes, oils, fatty soaps can also be used advantageously within the present invention

Alkoxylated Quaternary Ammonium (AQA) Cationic Surfactant

15 The second essential component of the present invention comprises an effective amount of an AQA surfactant of the formula:

$$\begin{array}{c} \text{R}^1 \\ | \\ \text{R}^2 \quad \text{N}^+ \quad \text{ApR}^4 \\ | \quad | \\ \text{R}^3 \quad \text{X}^- \end{array}$$

wherein R¹ is a linear, branched or substituted alkyl, alkenyl, aryl, alkaryl, ether or glycidyl ether moiety containing from 8 to 18 carbon atoms, preferably 8 to 16 carbon atoms, most preferably from 8 to 14 carbon atoms; R² and R³ are each independently alkyl groups containing from 1 to 3 carbon atoms, preferably methyl; R⁴ is selected from hydrogen (preferred), methyl and ethyl, X⁻ is an anion such as chloride, bromide, methylsulfate, sulfate to provide electrical neutrality; A is selected from C₁-C₄ alkoxy, especially ethoxy (i.e., -CH₂CH₂O-), propoxy, butoxy and mixtures thereof; and p is an integer from 2 to 30, preferably 2 to 15, more preferably 2 to 8, most preferably 2 to 4.

30 AQA compounds wherein the hydrocarbyl substituent R¹ is C₈-C₁₂ especially C₈-10, enhance the rate of dissolution of laundry granules, especially under cold water conditions, as compared with the higher chain length materials. Accordingly, the C₈-C₁₂ AQA surfactants may be preferred by some formulators. The levels of the AQA

surfactants used to prepare finished laundry detergent compositions can range from 0.1% to 5%, typically from 0.45% to 2.5%, by weight.

The present invention employs an "effective amount" of the AQA surfactants to improve the performance of cleaning compositions which contain other adjunct ingredients. By an "effective amount" of the AQA surfactants and adjunct ingredients herein is meant an amount which is sufficient to improve, either directionally or significantly at the 90% confidence level, the performance of the cleaning composition against at least some of the target soils and stains. Thus, in a composition whose targets include certain food stains, the formulator will use sufficient AQA to at least directionally improve cleaning performance against such stains. Likewise, in a composition whose targets include clay soil, the formulator will use sufficient AQA to at least directionally improve cleaning performance against such soil. Importantly, in a fully-formulated laundry detergent the AQA surfactants can be used at levels which provide at least a directional improvement in cleaning performance over a wide variety of soils and stains, as will be seen from the data presented hereinafter.

As noted, the AQA surfactants are used herein in detergent compositions in combination with other detergents surfactants at levels which are effective for achieving at least a directional improvement in cleaning performance. In the context of a fabric laundry composition, such "usage levels" can vary depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the volume of wash water and the type of washing machine.

For example, in a top-loading, vertical axis U.S.-type automatic washing machine using 45 to 83 liters of water in the wash bath, a wash cycle of 10 to 14 minutes and a wash water temperature of 10°C to 50°C, it is preferred to include from 2 ppm to 50 ppm, preferably from 5 ppm to 25 ppm, of the AQA surfactant in the wash liquor. On the basis of usage rates of from 50 ml to 150 ml per wash load, this translates into an in-product concentration (wt.) of the AQA surfactant of from 0.1% to 3.2%, preferably 0.3% to 1.5%, for a heavy-duty liquid laundry detergent. On the basis of usage rates of from 60 g to 95 g per wash load, for dense ("compact") granular laundry detergents (density above 650 g/l) this translates into an in-product concentration (wt.) of the AQA surfactant of from 0.2% to 5.0%, preferably from 0.5% to 2.5%. On the basis of usage rates of from 80 g to 100 g per load for spray-dried granules (i.e., "fluffy";

density below 650 g/l), this translates into an in-product concentration (wt.) of the AQA surfactant of from 0.1% to 3.5%, preferably from 0.3% to 1.5%.

For example, in a front-loading, horizontal-axis European-type automatic washing machine using 8 to 15 liters of water in the wash bath, a wash cycle of 10 to 60 minutes and a wash water temperature of 30°C to 95°C, it is preferred to include from 13 ppm to 900 ppm, preferably from 16 ppm to 390 ppm, of the AQA surfactant in the wash liquor. On the basis of usage rates of from 45 ml to 270 ml per wash load, this translates into an in-product concentration (wt.) of the AQA surfactant of from 0.4% to 5 2.64%, preferably 0.55% to 1.1%, for a heavy-duty liquid laundry detergent. On the basis of usage rates of from 40 g to 210 g per wash load, for dense ("compact") granular laundry detergents (density above 650 g/l) this translates into an in-product concentration (wt.) of the AQA surfactant of from 0.5 % to 3.5 %, preferably from 0.7 % to 1.5 %. On the basis of usage rates of from 140 g to 400 g per load for spray-10 dried granules (i.e., "fluffy"; density below 650 g/l), this translates into an in-product concentration (wt.) of the AQA surfactant of from 0.13% to 1.8%, preferably from 0.18% to 0.76%.
15

For example, in a top-loading, vertical-axis Japanese-type automatic washing machine using 26 to 52 liters of water in the wash bath, a wash cycle of 8 to 15 minutes and a wash water temperature of 5°C to 25°C, it is preferred to include from 1.67 ppm to 20 66.67 ppm, preferably from 3 ppm to 6 ppm, of the AQA surfactant in the wash liquor. On the basis of usage rates of from 20 ml to 30 ml per wash load, this translates into an in-product concentration (wt.) of the AQA surfactant of from 0.25% to 10%, preferably 1.5% to 2%, for a heavy-duty liquid laundry detergent. On the basis of usage rates of from 18 g to 35 g per wash load, for dense ("compact") granular laundry detergents (density above 650 g/l) this translates into an in-product concentration (wt.) of the AQA surfactant of from 0.25% to 10%, preferably from 0.5% to 1.0%. On the basis of usage rates of from 30 g to 40 g per load for spray-dried granules (i.e., 25 "fluffy"; density below 650 g/l), this translates into an in-product concentration (wt.) of the AQA surfactant of from 0.25% to 10%, preferably from 0.5% to 1%.
30

As can be seen from the foregoing, the amount of AQA surfactant used in a machine-wash laundering context can vary, depending on the habits and practices of the user, the type of washing machine, and the like. In this context, however, one heretofore unappreciated advantage of the AQA surfactants is their ability to provide at least 35

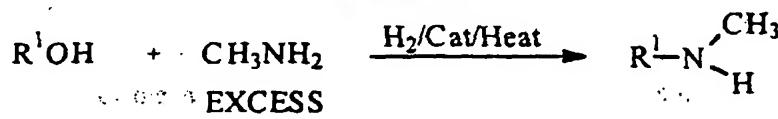
directional improvements in performance over a spectrum of soils and stains even when used at relatively low levels with respect to the other surfactants (generally anionics or anionic/nonionic mixtures) in the finished compositions. This is to be distinguished from other compositions of the art wherein various cationic surfactants are used with anionic surfactants at or near stoichiometric levels. In general, in the practice of this invention, the weight ratio of AQA:anionic surfactant in laundry compositions is in the range from 1:70 to 1:2, preferably from 1:40 to 1:6, more preferably from 1:30 to 1:6, most preferably from 1:15 to 1:8. In laundry compositions which comprise both anionic and nonionic surfactants, the weight ratio of AQA:mixed anionic/nonionic is in the range from 1:80 to 1:2, preferably 1:50 to 1:8.

Various other cleaning compositions which comprise an anionic surfactant, an optional nonionic surfactant and specialized surfactants such as betaines, sultaines, amine oxides, and the like, can also be formulated using an effective amount of the AQA surfactants in the manner of this invention. Such compositions include, but are not limited to, hand dishwashing products (especially liquids or gels), hard surface cleaners, shampoos, personal cleansing bars, laundry bars, and the like. Since the habits and practices of the users of such compositions show minimal variation, it is satisfactory to include from 0.25% to 5%, preferably from 0.45% to 2%, by weight, of the AQA surfactants in such compositions. Again, as in the case of the granular and liquid laundry compositions, the weight ratio of the AQA surfactant to other surfactants present in such compositions is low, i.e., sub-stoichiometric in the case of anionics. Preferably, such cleaning compositions comprise AQA/surfactant ratios as noted immediately above for machine-use laundry compositions.

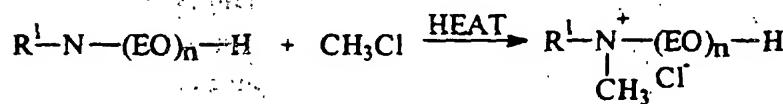
In contrast with other cationic surfactants known in the art, the alkoxylated cationics herein have sufficient solubility that they can be used in combination with mixed surfactant systems which are quite low in nonionic surfactants and which contain, for example, alkyl sulfate surfactants. This can be an important consideration for formulators of detergent compositions of the type which are conventionally designed for use in top loading automatic washing machines, especially of the type used in North America as well as under Japanese usage conditions. Typically, such compositions will comprise an anionic surfactant:nonionic surfactant weight ratio in the range from 25:1 to 1:25, preferably 20:1 to 3:1. This can be contrasted with European-type formulas which typically will comprise anionic:nonionic ratios in the range of 10:1 to 1:10, preferably 5:1 to 1:1.

The preferred ethoxylated cationic surfactants herein can be synthesized using a variety of different reaction schemes (wherein "EO" represents -CH₂CH₂O- units), as follows.

SCHEME 1

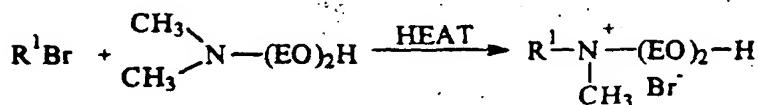
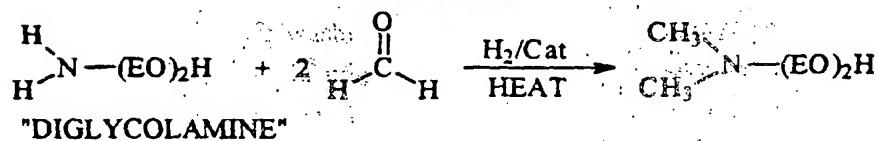


5

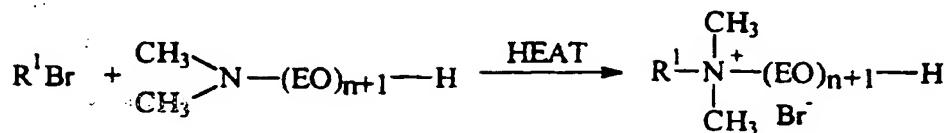
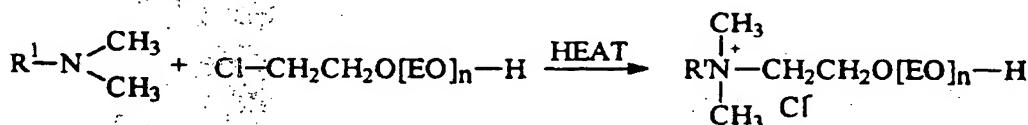
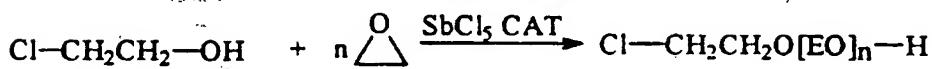


10

SCHEME 2

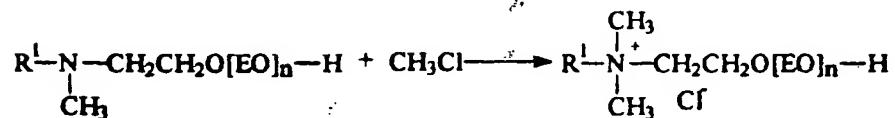


10

SCHEME 3SCHEME 4

5

An economical reaction scheme is as follows.

SCHEME 5

10

For reaction Scheme 5, the following parameters summarize the optional and preferred reaction conditions herein for step 1. Step 1 of the reaction is preferably conducted in an aqueous medium. Reaction temperatures are typically in the range of 100-230°C. Reaction pressures are 50-1000 psig. A base, preferably sodium hydroxide, can be used to react with the HSO_4^- generated during the reaction. In another mode, an excess of the amine can be employed to also react with the acid. The mole ratio of amine to alkyl sulfate is typically from 10:1 to 1:1.5; preferably from 5:1 to 1:1.1;

15

more preferably from 2:1 to 1:1. In the product recovery step, the desired substituted amine is simply allowed to separate as a distinct phase from the aqueous reaction medium in which it is insoluble. The product of step 1 is then ethoxylated and quaternized using standard reactions, as shown.

5

The following illustrates the foregoing for the convenience of the formulator, but is not intended to be limiting thereof.

Preparation of N-(2-hydroxyethyl)-N-methyldodecylamine - To a glass autoclave liner 10 is added 156.15 g of sodium dodecyl sulfate (0.5415 moles), 81.34 g of 2-(methylamino)ethanol (1.083 moles), 324.5 g of distilled H₂O, and 44.3 g of 50 wt. % sodium hydroxide solution (0.5538 moles NaOH). The glass liner is sealed into 3 L, stainless steel, rocking autoclave, purged twice with 260 psig nitrogen and then heated to 160-180°C under 700-800 psig nitrogen for 3 hours. The mixture is cooled to room 15 temperature and the liquid contents of the glass liner are poured into a 1 L separatory funnel. The mixture is separated into a clear lower layer, turbid middle layer and clear upper layer. The clear upper layer is isolated and placed under full vacuum (<100 mm Hg) at 60-65°C with mixing to remove any residual water. The clear liquid turns cloudy upon removing residual water as additional salts crystallizes out. The liquid is 20 vacuum filtered to remove salts to again obtain a clear, colorless liquid. After a few days at room temperature, additional salts crystallize and settle out. The liquid is vacuum filtered to remove solids and again a clear, colorless liquid is obtained which remains stable. The isolated clear, colorless liquid is the title product by NMR analysis and is >90% by GC analysis with a typical recovery of >90%. The amine is then 25 ethoxylated in standard fashion. Quaternization with an alkyl halide to form the AQA surfactants herein is routine.

According to the foregoing, the following are nonlimiting, specific illustrations of AQA surfactants used herein. It is to be understood that the degree of alkoxylation noted 30 herein for the AQA surfactants is reported as an average, following common practice for conventional ethoxylated nonionic surfactants. This is because the ethoxylation reactions typically yield mixtures of materials with differing degrees of ethoxylation. Thus, it is not uncommon to report total EO values other than as whole numbers, e.g., "EO2.5", "EO3.5", and the like.

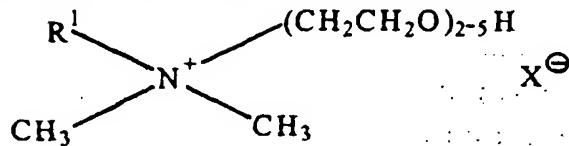
35

<u>Designation</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>Alkoxylation</u>
--------------------	----------------------	----------------------	----------------------	---------------------

	AQA-1	C ₁₂ -C ₁₄	CH ₃	CH ₃	EO2
5	AQA-2	C ₁₀ -C ₁₆	CH ₃	CH ₃	EO2
	AQA-3	C ₁₂	CH ₃	CH ₃	EO2
10	AQA-4	C ₁₄	CH ₃	CH ₃	EO2-3
	AQA-5	C ₁₀ -C ₁₈	CH ₃	CH ₃	EO5-8
15	AQA-6	C ₁₂ -C ₁₄	C ₂ H ₅	CH ₃	EO3-5
	AQA-7	C ₁₄ -C ₁₆	CH ₃	C ₃ H ₇	(EO/PrO)4
20	AQA-8	C ₁₂ -C ₁₄	CH ₃	CH ₃	(PrO)3
	AQA-9	C ₁₂ -C ₁₈	CH ₃	CH ₃	EO10
25	AQA-10	C ₈ -C ₁₈	CH ₃	CH ₃	EO15
	AQA-11	C ₁₀	C ₂ H ₅	C ₂ H ₅	EO3.5
30	AQA-12	C ₁₀	CH ₃	CH ₃	EO2.5
	AQA-13	C ₁₀	CH ₃	CH ₃	EO3.5
	AQA-14	C ₁₀	C ₄ H ₉	C ₄ H ₉	EO30
35	AQA-15	C ₈ C ₁₄	CH ₃	CH ₃	EO2
	AQA-16	C ₁₀	CH ₃	CH ₃	EO10
	AQA-17	C ₁₂ -C ₁₈	C ₃ H ₉	C ₃ H ₇	Bu ₄
	AQA-18	C ₁₂ -C ₁₈	CH ₃	CH ₃	EO5

AQA-19	C ₈	CH ₃	CH ₃	iPr ₃
AQA-20	C ₈	CH ₃	CH ₃	EO3-7
5				
AQA-21	C ₁₂	CH ₃	CH ₃	EO3.5
AQA-22	C ₁₂	CH ₃	CH ₃	EO4.5

10 Highly preferred AQA compound for use herein are of the formula



wherein R¹ is C₈-C₁₈ hydrocarbyl and mixtures thereof, especially C₈-C₁₄ alkyl, preferably C₈, C₁₀ and C₁₂ alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

15

As noted, compounds of the foregoing type include those wherein the ethoxy (CH₂CH₂O) units (EO) are replaced by butoxy, isopropoxy [CH(CH₃)CH₂O] and [CH₂CH(CH₃O)] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

20

A highly preferred AQA compound for use in under built formulations are of the formula wherein p is an integer in the range of between 10 and 15. This compound is particularly useful in laundry handwash detergent compositions.

25 Non-AOA Detergent Surfactants

In addition to the AQA surfactant, the compositions of the present invention preferably further comprise a non-AQA surfactant. Non-AQA surfactants may include essentially any anionic, nonionic or additional cationic surfactant.

30

Anionic Surfactant

Nonlimiting examples of anionic surfactants useful herein typically at levels from 1% to 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary ("AS"), branched-chain and random C₁₀-C₂₀ alkyl sulfates, the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and 5 CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₂-C₁₈ alpha-sulfonated fatty acid esters, the C₁₀-C₁₈ sulfated polyglycosides, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), and the C₁₀-C₁₈ alkyl alkoxy 10 carboxylates (especially the EO 1-5 ethoxycarboxylates). The C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, can also be included in the overall compositions. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Other conventional useful surfactants are listed in standard texts.

15

Nonionic Surfactants

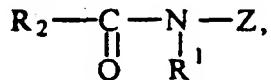
Nonlimiting examples of nonionic surfactants useful herein typically at levels from 1% to 55%, by weight include the alkoxylated alcohols (AE's) and alkyl phenols, 20 polyhydroxy fatty acid amides (PFAA's), alkyl polyglycosides (APG's), C₁₀-C₁₈ glycerol ethers.

More specifically, the condensation products of primary and secondary aliphatic alcohols with from 1 to 25 moles of ethylene oxide (AE) are suitable for use as the 25 nonionic surfactant in the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms, more preferably from 10 to 18 carbon atoms, with from 1 to 10 moles, preferably 2 to 7, most preferably 2 to 5, of ethylene 30 oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include: TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide) and TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; 35 NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol

with 3 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide) and NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company; KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company; and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. The preferred range of HLB in these AE nonionic surfactants is from 8-11 and most preferred from 8-10. Condensates with propylene oxide and butylene oxides may also be used.

10

Another class of preferred nonionic surfactants for use herein are the polyhydroxy fatty acid amide surfactants of the formula:



15

wherein R¹ is H, or C₁-4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅-31 hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R¹ is methyl, R² is a straight C₁₁-15 alkyl or C₁₅-17 alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction. Typical examples include the C₁₂-C₁₈ and C₁₂-C₁₄ N-methylglucamides. See U.S. 5,194,639 and 5,298,636. N-alkoxy polyhydroxy fatty acid amides can also be used; see U.S. 5,489,393.

20

Also useful as the nonionic surfactant in the present invention are the alkylpolysaccharides such as those disclosed in U.S. Patent 4,565,647, Lienado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms, preferably from 10 to 16 carbon atoms, and a polysaccharide, e.g. a polyglycoside, 25 hydrophilic group containing from 1.3 to 10, preferably from 1.3 to 3, most preferably from 1.3 to 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the

additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula:

5



wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to 10, preferably 0; and x is from 1.3 to 10, preferably from 1.3 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position).
15 The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are also suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from 6 to 14 carbon atoms, preferably from 8 to 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from 2 to 25 moles, more preferably from 3 to 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to 30 as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant in the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from 1500 to 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this

hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is 50% of the total weight of the condensation product, which corresponds to condensation with up to 40 moles of ethylene oxide. Examples of 5 compounds of this type include certain of the commercially-available PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product 10 resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from 2500 to 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from 40% to 80% by weight of polyoxyethylene and has a molecular 15 weight of from 5,000 to 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Additional Cationic surfactants

20 Suitable cationic surfactants are preferably water dispersible compound having surfactant properties comprising at least one ester (ie -COO-) linkage and at least one cationically charged group.

Other suitable cationic surfactants include the quaternary ammonium surfactants 25 selected from mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Other suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

Optional Detergent Ingredients

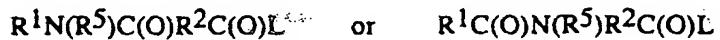
The following illustrates various other optional ingredients which may be used in the compositions of this invention, but is not intended to be limiting thereof.

Bleach Activators

Bleach activators are preferred components of the composition of the present invention. Where present, the amount of bleach activators will typically be at a level of from 0.1% to 60%, more typically from 0.5% to 40% of the bleaching composition comprising the
5 bleaching agent-plus-bleach activator.

The combination of peroxygen bleaching agents, such as percarbonate and bleach activators results in the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting
10 examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful
herein.
15

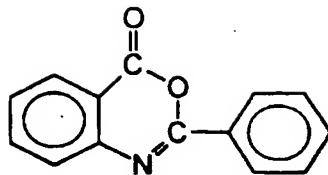
Highly preferred amido-derived bleach activators are those of the formulae:



20 wherein R^1 is an alkyl group containing from 6 to 12 carbon atoms, R^2 is an alkylene containing from 1 to 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from 1 to 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is
25 phenyl sulfonate.

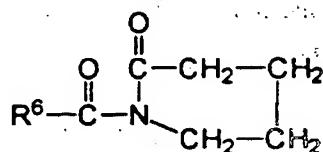
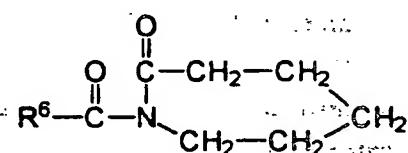
Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nanonamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S.
30 Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:
35



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:

5



10 wherein R⁶ is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 15 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

20 **Bleach Catalyst**

Bleach catalysts are preferred components of the compositions of the present invention. If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the 25 manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1,

549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include Mn^{IV}₂(u-O)₃(1,4,7-trimethyl-1,4,7-triazacyclononane)₂(PF₆)₂, Mn^{III}₂(u-O)₁(u-OAc)₂(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(ClO₄)₂, Mn^{IV}₄(u-O)₆(1,4,7-triazacyclononane)₄(ClO₄)₄, Mn^{III}Mn^{IV}₄(u-O)₁(u-OAc)₂-(1,4,7-trimethyl-1,4,7-triazacyclononane)₂(ClO₄)₃, Mn^{IV}(1,4,7-trimethyl-1,4,7-triazacyclononane)-(OCH₃)₃(PF₆), and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 10 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide 15 from 0.1 ppm to 700 ppm, more preferably from 1 ppm to 500 ppm, of the catalyst species in the laundry liquor.

Cobalt bleach catalysts useful herein are known, and are described, for example, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula [Co(NH₃)₅OAc]^{T_y}, wherein "OAc" represents an acetate moiety and "T_y" is an anion, and especially cobalt pentaamine acetate chloride, [Co(NH₃)₅OAc]Cl₂; as well as [Co(NH₃)₅OAc](OAc)₂; [Co(NH₃)₅OAc](PF₆)₂; [Co(NH₃)₅OAc](SO₄); [Co(NH₃)₅OAc](BF₄)₂; and 25 [Co(NH₃)₅OAc](NO₃)₂ (herein "PAC").

These cobalt catalysts are readily prepared by known procedures, such as taught for example in the Tobe article and the references cited therein, in U.S. Patent 4,810,410, to Diakun et al, issued March 7, 1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The 30 Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

35 As a practical matter, and not by way of limitation, the automatic dishwashing compositions and cleaning processes herein can be adjusted to provide on the order of at

least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from 0.01 ppm to 25 ppm, more preferably from 0.05 ppm to 10 ppm, and most preferably from 0.1 ppm to 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic dishwashing process, typical automatic dishwashing compositions herein will comprise from 0.0005% to 0.2%, more preferably from 0.004% to 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the cleaning compositions.

10 Additional Bleach

The detergent compositions herein may optionally comprise an additional bleaching agent. When present, such additional bleaching agents will typically be present at levels of from 1% to 30%, more typically from 5% to 20%, of the detergent composition, especially for fabric laundering.

20 The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

25 Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

35 Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium

peroxide. Perborate bleach, persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

Bleaching agents other than oxygen bleaching agents are also known in the art and can
5 be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al.
If used, detergent compositions will typically contain from 0.025% to 1.25%, by
weight, of such bleaches, especially sulfonate zinc phthalocyanine.
10 Mixtures of bleaching agents can also be used.

Builders

15 Detergent builders can optionally, but preferably be included in the compositions herein, for example to assist in controlling mineral, especially Ca^{2+} and/or Mg^{2+} , hardness in wash water or to assist in the removal of particulate soils from surfaces. Builders can operate via a variety of mechanisms including forming soluble or insoluble complexes with hardness ions, by ion exchange, and by offering a surface more
20 favorable to the precipitation of hardness ions than are the surfaces of articles to be cleaned. Builder level can vary widely depending upon end use and physical form of the composition. Built detergents typically comprise at least 1% builder. Liquid formulations typically comprise 5% to 50%, more typically 5% to 35% of builder. Granular formulations typically comprise from 10% to 80%, more typically 15% to
25 50% builder by weight of the detergent composition. Lower or higher levels of builders are not excluded. For example, certain detergent additive or high-surfactant formulations can be unbuilt.

30 Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; silicates including water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional-structure as well as amorphous-solid or non-structured-liquid types; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate; aluminosilicates; organic mono-, di-, tri-, and tetracarboxylates
35 especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular

weight polymer carboxylates including aliphatic and aromatic types; and phytic acid. These may be complemented by borates, e.g., for pH-buffering purposes, or by sulfates, especially sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or builder-containing detergent compositions.

Builder mixtures, sometimes termed "builder systems" can be used and typically comprise two or more conventional builders, optionally complemented by chelants, pH-buffers or fillers, though these latter materials are generally accounted for separately

10 when describing quantities of materials herein. In terms of relative quantities of surfactant and builder in the present detergents, preferred builder systems are typically formulated at a weight ratio of surfactant to builder of from 60:1 to 1:80. Certain preferred laundry detergents have said ratio in the range 0.90:1.0 to 4.0:1.0, more preferably from 0.95:1.0 to 3.0:1.0.

15 P-containing detergent builders often preferred where permitted by legislation include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates exemplified by the tripolyphosphates, pyrophosphates, glassy polymeric meta-phosphates; and phosphonates.

20 Suitable silicate builders include alkali metal silicates, particularly those liquids and solids having a SiO₂:Na₂O ratio in the range 1.6:1 to 3.2:1, including, particularly for automatic dishwashing purposes, solid hydrous 2-ratio silicates marketed by PQ Corp. under the tradename BRITESIL®, e.g., BRITESIL H2O; and layered silicates, e.g.,

25 those described in U.S. 4,664,839, May 12, 1987, H. P. Rieck. NaSKS-6, sometimes abbreviated "SKS-6", is a crystalline layered aluminium-free δ-Na₂SiO₅ morphology silicate marketed by Hoechst and is preferred especially in granular laundry compositions. See preparative methods in German DE-A-3,417,649 and DE-A-3,742,043. Other layered silicates, such as those having the general formula

30 NaMSi_xO_{2x+1·yH₂O} wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0, can also or alternately be used herein. Layered silicates from Hoechst also include NaSKS-5, NaSKS-7 and NaSKS-11, as the α, β and γ layer-silicate forms. Other silicates may also be useful, such as magnesium silicate, which can serve as a crispening agent in granules, as a

35 stabilising agent for bleaches, and as a component of suds control systems.

Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof having chain structure and a composition represented by the following general formula in an anhydride form: $xM_2O_ySiO_2.zM'O$ wherein M is Na and/or K, M' is Ca and/or Mg; y/x is 0.5 to 2.0 and z/x is 0.005 to 1.0 as taught in U.S.

5 5,427,711, Sakaguchi et al, June 27, 1995.

Suitable carbonate builders include alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973, although sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, and other carbonate minerals such as trona or any convenient multiple salts of sodium carbonate and calcium carbonate such as those having the composition $2Na_2CO_3.CaCO_3$ when anhydrous, and even calcium carbonates including calcite, aragonite and vaterite, especially forms having high surface areas relative to compact calcite may be useful, for example as seeds or for use in synthetic detergent bars.

10 15 Aluminosilicate builders are especially useful in granular detergents, but can also be incorporated in liquids, pastes or gels. Suitable for the present purposes are those having empirical formula: $[M_z(AlO_2)_z(SiO_2)_v]xH_2O$ wherein z and v are integers of at least 6, the molar ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264. Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically derived. An aluminosilicate production method is in U.S. 3,985,669, Krummel, et al, October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from Zeolite P, the so-called Zeolite MAP. Natural types, including 20 25 clinoptilolite, may be used. Zeolite A has the formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$ wherein x is from 20 to 30, especially 27. Dehydrated zeolites (x = 0 - 10) may also be used. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

30 35 Suitable organic detergent builders include polycarboxylate compounds, including water-soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates. Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form. When in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Polycarboxylate builders include the ether polycarboxylates, such as oxydisuccinate, see Berg, U.S. 3,128,287, April 7,

1964, and Lamberti et al, U.S. 3,635,830, January 18, 1972; "TMS/TDS" builders of U.S. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

5

Other suitable builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid; as well as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

10

Citrates, e.g., citric acid and soluble salts thereof are important carboxylate builders 15 e.g., for heavy duty liquid detergents, due to availability from renewable resources and biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicates. Oxydisuccinates are also especially useful in such compositions and combinations.

20

Where permitted, and especially in the formulation of bars used for hand-laundering operations, alkali metal phosphates such as sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates, e.g., those of U.S. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137 can also be used and 25 may have desirable antiscalting properties.

25

Certain detergents surfactants or their short-chain homologs also have a builder action. For unambiguous formula accounting purposes, when they have surfactant capability, these materials are summed up as detergents surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush, January 28, 1986. Succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. Succinate builders also include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate. Lauryl-succinates are 35 described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated

into the compositions as surfactant/builder materials alone or in combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide additional builder activity. Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al, March 13, 1979 and in U.S. 3,308,067, Diehl, March 7, 5 1967. See also Diehl, U.S. 3,723,322.

Other types of inorganic builder materials which can be used have the formula $(M_x)_y(CO_3)_z$ wherein x and i are integers from 1 to 15, y is an integer from 1 to 10, z is an integer from 2 to 25, M_i are cations, at least one of which is a water-soluble, and 10 the equation $\sum_i = 1-15(x_i \text{ multiplied by the valence of } M_i) + 2y = 2z$ is satisfied such that the formula has a neutral or "balanced" charge. These builders are referred to herein as "Mineral Builders". Waters of hydration or anions other than carbonate may be added provided that the overall charge is balanced or neutral. The charge or valence effects of such anions should be added to the right side of the above equation.

15 Preferably, there is present a water-soluble cation selected from the group consisting of hydrogen, water-soluble metals, hydrogen, boron, ammonium, silicon, and mixtures thereof, more preferably, sodium, potassium, hydrogen, lithium, ammonium and mixtures thereof, sodium and potassium being highly preferred. Nonlimiting examples of noncarbonate anions include those selected from the group consisting of chloride, sulfate, fluoride, oxygen, hydroxide, silicon dioxide, chromate, nitrate, borate and mixtures thereof. Preferred builders of this type in their simplest forms are selected 20 from the group consisting of $Na_2Ca(CO_3)_2$, $K_2Ca(CO_3)_2$, $Na_2Ca_2(CO_3)_3$, $NaKCa(CO_3)_2$, $NaKCa_2(CO_3)_3$, $K_2Ca_2(CO_3)_3$, and combinations thereof. An especially preferred material for the builder described herein is $Na_2Ca(CO_3)_2$ in any of 25 its crystalline modifications. Suitable builders of the above-defined type are further illustrated by, and include, the natural or synthetic forms of any one or combinations of the following minerals: Afghanite, Andersonite, AshcroftineY, Beyerite, Borcarite, Burbankite, Butschliite, Cancrinite, Carbocermaite, Carletonite, Davyne, DonnayiteY, Fairchildite, Ferrisurite, Franzinite, Gaudefroyite, Gaylussite, Girvasite, Gregoryite, 30 Jouravskite, KamphaugiteY, Kettnerite, Khanneshite, LepersonniteGd, Liottite, McKelveyiteY, Microsommitte, Mroseite, Natrofairchildite, Nyerereite, RemonditeCe, Sacrofanite, Schrockingerite, Shortite, Surite, Tunisite, Tuscanite, Tyrolite, Vishnevite, and Zemkorite. Preferred mineral forms include Nyererite, Fairchildite and Shortite.

35 Enzymes

Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition. Preferred detergative enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases and peroxidases. Highly preferred for automatic dishwashing are amylases and/or proteases.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware. In practical terms for current commercial preparations, typical amounts are up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For certain detergents, such as in automatic dishwashing, it may be desirable to increase the active enzyme content of the commercial preparation in order to minimize the total amount of non-catalytically active materials and thereby improve spotting/filming or other end-results. Higher active levels may also be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12,

developed and sold as ESPERASE by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, both filed October 13, 1994.

Amylases suitable herein, especially for, but not limited to automatic dishwashing purposes, include, for example, α-amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents such as automatic dishwashing types, especially improved oxidative stability as

measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetyl ethylenediamine in
5 buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as 60°C; or alkaline stability, e.g., at a pH from 8 to 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor
10 International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* α-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in
15 bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B. licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B. subtilis*, or *B. stearothermophilus*; (b) stability-enhanced amylases as described by Genencor
20 International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C.
25 Hutchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B. licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly
30 important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative
35 stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced

amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

- 5 Other amylase enzymes include those described in WO 95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056. Specific amylase enzymes for use in the detergent compositions of the present invention include α -amylases characterized by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10,
- 10 measured by the Phadebas® α -amylase activity assay. (Such Phadebas® α -amylase activity assay is described at pages 9-10, WO 95/26397.) Also included herein are α -amylases which are at least 80% homologous with the amino acid sequences shown in the SEQ ID listings in the references. These enzymes are preferably incorporated into laundry detergent compositions at a level from 0.00018% to 0.060% pure enzyme by weight of the total composition; more preferably from 0.00024% to 0.048% pure enzyme by weight of the total composition.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, Barbesgaard et al, March 6, 1984, discloses suitable fungal cellulases from *Hunicola insolens* or *Hunicolla* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Hunicola lanuginosa* and commercially available from Novo, see

also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

5 In spite of the large number of publications on lipase enzymes, only the lipase derived from *Humicola lanuginosa* and produced in *Aspergillus oryzae* as host has so far found widespread application as additive for fabric washing products. It is available from Novo Nordisk under the tradename Lipolase, as noted above. In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants.

10 As described in WO 92/05249, the D96L variant of the native *Humicola lanuginosa* lipase improves the lard stain removal efficiency by a factor 4.4 over the wild-type lipase (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter). Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk discloses that the lipase variant (D96L) may be added in an amount corresponding to 15 0.001-100- mg (5-500,000 LU/liter) lipase variant per liter of wash liquor. The present invention provides the benefit of improved whiteness maintenance on fabrics using levels of D96L variant in detergent compositions containing the AQA surfactants in the manner disclosed herein, especially when the D96L is used at levels in the range of 50 LU to 8500 LU per liter of wash solution.

20 Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or

25 prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

30 A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18,

35 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are

disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems 5 are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Enzyme Stabilizing System

10 The enzyme-containing compositions herein may optionally also comprise from 0.001% to 10%, preferably from 0.005% to 8%, most preferably from 0.01% to 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergative enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the 15 formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

20

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Typical detergent compositions, 25 especially liquids, will comprise from 1 to 30, preferably from 2 to 20, more preferably from 8 to 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting 30 action of certain types of surfactant.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced levels of total boron in detergent compositions may be possible through the use of such substituted boron derivatives.

10 Stabilizing systems of certain cleaning compositions, for example automatic dishwashing compositions, may further comprise from 0 to 10%, preferably from 0.01% to 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be

15 small, typically in the range from 0.5 ppm to 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during dish- or fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in use is sometimes problematic. Since percarbonate has the ability to react with chlorine bleach the use of additional stabilizers against chlorine, may, most generally, not be

20 essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetraacetic acid (EDTA) or alkali metal salt thereof, monoethanolamine

25 (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate,

30 acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will

35

exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in US 4,652,392, Baginski et al.

Polymeric Soil Release Agent

10 Known polymeric soil release agents, hereinafter "SRA" or "SRA's", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the composition.

15 Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with SRA to be more easily cleaned in later washing procedures.

SRA's can include a variety of charged, e.g., anionic or even cationic (see U.S. 4,956,447), as well as noncharged monomer units and structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

25 Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without of course forming a densely crosslinked overall structure.

30 35 Suitable SRA's include: a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat

units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink: such ester oligomers can be prepared by (a) ethoxylating allyl alcohol, (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/ oligomerization procedure and (c) reacting the product of (b) with sodium metabisulfite in water; the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al, for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"); the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al, the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; and the C₁-C₄ alkylcelluloses and C₄ hydroxyalkyl celluloses; see U.S. 4,000,093, December 28, 1976 to Nicol, et al. Suitable SRA's characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available examples include SOKALAN SRA's such as SOKALAN HP-22, available from BASF, Germany. Other SRA's are polyesters with repeat units containing 10-15% by weight of ethylene terephthalate together with 90-80% by weight of polyoxyethylene terephthalate, derived from a

polyoxyethylene glycol of average molecular weight 300-5,000. Commercial examples include ZELCON 5126 from Dupont and MILEASE T from ICI.

Another preferred SRA is an oligomer having empirical formula
5 $(\text{CAP})_2(\text{EG/PG})_5(\text{T})_5(\text{SIP})_1$ which comprises terephthaloyl (T), sulfoisophthaloyl (SIP), oxyethyleneoxy and oxy-1,2-propylene (EG/PG) units and which is preferably terminated with end-caps (CAP), preferably modified isethionates, as in an oligomer comprising one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a defined ratio, preferably 0.5:1 to 10:1, and two end-cap
10 units derived from sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said SRA preferably further comprises from 0.5% to 20%, by weight of the oligomer, of a crystallinity-reducing stabiliser, for example an anionic surfactant such as linear sodium dodecylbenzenesulfonate or a member selected from xylene-, cumene-, and toluene-sulfonates or mixtures thereof, these stabilizers or modifiers being introduced into the
15 synthesis pot, all as taught in U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995. Suitable monomers for the above SRA include Na 2-(2-hydroxyethoxy)-ethanesulfonate, DMT, Na-dimethyl 5-sulfoisophthalate, EG and PG.

Yet another group of preferred SRA's are oligomeric esters comprising: (1) a backbone comprising (a) at least one unit selected from the group consisting of dihydroxysulfonates, polyhydroxy sulfonates, a unit which is at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, and combinations thereof; (b) at least one unit which is a terephthaloyl moiety; and (c) at least one unsulfonated unit which is a 1,2-oxyalkyleneoxy moiety; and (2) one or more capping units selected from nonionic capping units, anionic capping units such as alkoxylated, preferably ethoxylated, isethionates, alkoxylated propanesulfonates, alkoxylated propanedisulfonates, alkoxylated phenolsulfonates, sulfoaroyl derivatives and mixtures thereof. Preferred of such esters are those of empirical formula:
20 $\{(\text{CAP})_x(\text{EG/PG})_y'(\text{DEG})_y''(\text{PEG})_y'''(\text{T})_z(\text{SIP})_z'(\text{SEG})_q(\text{B})_m\}$
25

30 wherein CAP, EG/PG, PEG, T and SIP are as defined hereinabove, (DEG) represents di(oxyethylene)oxy units; (SEG) represents units derived from the sulfoethyl ether of glycerin and related moiety units; (B) represents branching units which are at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone; x is from 1 to 12; y' is from 0.5 to 25; y'' is from 0 to 12; y''' is from 0 to 10; y'+y''+y''' totals from 0.5 to 25; z is from 1.5 to 25; z' is from 0 to 12; z + z'
35

totals from 1.5 to 25; q is from 0.05 to 12; m is from 0.01 to 10; and x, y', y'', y''', z, z', q and m represent the average number of moles of the corresponding units per mole of said ester and said ester has a molecular weight ranging from 500 to 5,000.

5 Preferred SEG and CAP monomers for the above esters include Na-2-(2,3-dihydroxypropoxy)ethanesulfonate ("SEG"), Na-2-[2-(2-hydroxyethoxy) ethoxy]ethanesulfonate ("SE3") and its homologs and mixtures thereof and the products of ethoxylating and sulfonating allyl alcohol. Preferred SRA esters in this class include the product of transesterifying and oligomerizing sodium 2-[2-(2-hydroxyethoxy)ethoxy]ethanesulfonate and/or sodium 2-[2-[2-(2-hydroxyethoxy)-ethoxy]ethoxy]ethanesulfonate, DMT, sodium 2-(2,3-dihydroxypropoxy) ethane sulfonate, EG, and PG using an appropriate Ti(IV) catalyst and can be designated as (CAP)2(T)5(EG/PG)1.4(SEG)2.5(B)0.13 wherein CAP is (Na⁺-O₃S(CH₂CH₂O)₃.5)- and B is a unit from glycerin and the mole ratio EG/PG is 1.7:1 as measured by conventional gas chromatography after complete hydrolysis.

Additional classes of SRA's include (I) nonionic terephthalates using diisocyanate coupling agents to link up polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With a proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.; (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.; (IV) poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF made, by grafting acrylic monomers on to sulfonated polyesters; these SRA's assertedly have soil release and anti-redeposition activity similar to known cellulose ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie; (VI) grafts of vinyl monomers such as acrylic acid and vinyl acetate on to proteins such as caseins, see EP 457,205 A to BASF (1991); (VII) polyester-polyamide SRA's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al, DE

2,335,044 to Unilever N. V., 1974. Other useful SRA's are described in U.S. Patents 4,240,918, 4,787,989, 4,525,524 and 4,877,896.

Clay Soil Removal/Anti-redeposition Agents

5

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from 0.01% to 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain 0.01% to 5%.

10

15

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylene-pentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. See U.S. Patent 4,891,160, VanderMeer, issued January 2, 1990 and WO 95/32272, published November 30, 1995. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

20

25

Polymeric Dispersing Agents

30

Polymeric dispersing agents can advantageously be utilized at levels from 0.1% to 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in

35

combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or

5 copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid.

10 The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of

15 polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from 2,000 to 10,000, more preferably from 4,000 to 7,000 and most preferably from 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in

20 detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of

25 copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from 2,000 to 100,000, more preferably from 5,000 to 75,000, most preferably from 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from 30:1 to 1:1, more preferably from 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid

30 copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents,

35 include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed

in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG
5 can exhibit dispersing agent performance as well as act as a clay soil removal-
antiredeposition agent. Typical molecular weight ranges for these purposes range from
500 to 100,000, preferably from 1,000 to 50,000, more preferably from 1,500 to
10,000.

10 Polyaspartate and polyglutamate dispersing agents may also be used, especially in
conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably
have a molecular weight (avg.) of 10,000.

Brightener

15 Any optical brighteners or other brightening or whitening agents known in the art can
be incorporated at levels typically from 0.01% to 1.2%, by weight, into the detergent
compositions herein. Commercial optical brighteners which may be useful in the
present invention can be classified into subgroups, which include, but are not
20 necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid,
methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring
heterocycles, and other miscellaneous agents. Examples of such brighteners are
disclosed in "The Production and Application of Fluorescent Brightening Agents", M.
Zahradnik, Published by John Wiley & Sons, New York (1982).

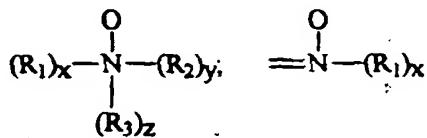
25 Specific examples of optical brighteners which are useful in the present compositions
are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988.
These brighteners include the PHORWHITE series of brighteners from Verona. Other
brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and
30 Tinopal SBM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the
2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes;
4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these
brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(benzimidazol-2-
yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-
35 naphtho[1,2-d]oxazole; and 2-(stilben-4-yl)-2H-naphtho[1,2-d]triazole. See also U.S.
Patent 3,646,015, issued February 29, 1972 to Hamilton.

Dye Transfer Inhibiting Agents

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from 0.01% to 10% by weight of the composition, preferably from 0.01% to 5%, and more preferably from 0.05% to 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: R-A_x-P; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)_x, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



25

wherein R₁, R₂, R₃ are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa < 10, preferably pKa < 7, more preferred pKa < 6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable

polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the
5 amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000
10 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of 50,000 and an amine to amine N-oxide ratio of 1:4.
15

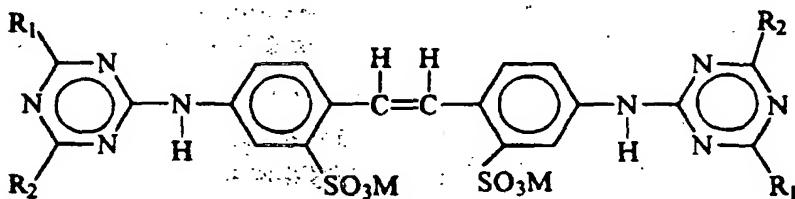
Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular
20 weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113, "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more
25 preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from 5,000 to 400,000, preferably from 5,000 to 200,000, and more preferably from 5,000 to 50,000. PVP's are known to persons
30 skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from 500 to 100,000, preferably from 1,000 to 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from 2:1 to 50:1, and more preferably from 3:1 to 10:1.

The detergent compositions herein may also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.01% to 1% by weight of such optical brighteners.

5

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



10

wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

15

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

20

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

25

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

30

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Chelating Agents

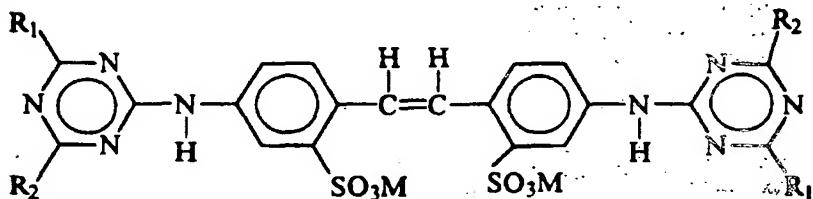
The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

The detergent compositions herein may also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.01% to 1% by weight of such optical brighteners.

5

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



10

wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

15

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

20

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

25

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylenediaminetriacetates, nitrolotriacetates, ethylenediamine tetrapropionate, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as

5 DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates.

If utilized, these chelating agents will generally comprise from 0.1% to 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from 0.1% to 3.0% by weight of such compositions.

25 **Suds Suppressors**

Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 30 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued

September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

5 The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monoaliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlorotriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of -40°C and 50°C, and a minimum boiling point not less than 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from 12 to 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as 30 polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 35 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

- 5 Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al., and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.
- 10 An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:
 - (i) polydimethylsiloxane fluid having a viscosity of from 20 cs. to 1,500 cs. at 25°C;
 - (ii) from 5 to 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(CH_3)_3SiO^{1/2}$ units of SiO_2 units in a ratio of from $(CH_3)_3SiO^{1/2}$ units and to SiO_2 units of from 0.6:1 to 1.2:1; and
 - (iii) from 1 to 20 parts per 100 parts by weight of (i) of a solid silica gel.In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.
- 15
- 20
- 25
- 30
- 35

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from 0.001 to 1, preferably from 0.01 to 0.7, most preferably from 0.05 to 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, 5,288,431, Huber et al., issued

February 22, 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

5 The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than 1,000, preferably between 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than 2 weight %, preferably more than 5 weight %.

10 The preferred solvent herein is polyethylene glycol having an average molecular weight of less than 1,000, more preferably between 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

15 The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

20 Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

25 30 For any detergent compositions to be used in automatic laundry or dishwashing machines, suds should not form to the extent that they either overflow the washing machine or negatively affect the washing mechanism of the dishwasher. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a

low-sudsing laundry or dishwashing detergents for use in automatic laundry or dishwashing machines.

The compositions herein will generally comprise from 0% to 10% of suds suppressor.
5 When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to 5%, by weight, of the detergent composition. Preferably, from 0.5% to 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is
10 practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from 0.01% to 1% of silicone suds suppressor is used, more preferably from 0.25% to 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from 0.1% to 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from 0.01% to 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

20 Alkoxylated Polycarboxylates

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described
25 in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula
- $(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The
30 molecular weight can vary, but is typically in the range of 2000 to 50,000. Such alkoxylated polycarboxylates can comprise from 0.05% to 10%, by weight, of the compositions herein.

35 Fabric Softeners

Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from 0.5% to 10% by weight in the present compositions to provide fabric softener benefits

5 concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981

10 Perfumes

Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from 0.01% to 2% by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise 20 from 0.0001% to 90% of a finished perfume composition.

Several perfume formulations are set forth in Example XI, hereinafter. Non-limiting examples of perfume ingredients useful herein include: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; ionone methyl; ionone gamma methyl; 25 methyl cedrylone; methyl dihydrojasmonate; methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; para-hydroxy-phenyl-butanone; benzophenone; methyl beta-naphthyl ketone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-30 carboxaldehyde; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecane; condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indol, condensation products of phenyl acetaldehyde and indol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; ethyl vanillin; heliotropin; hexyl cinnamic aldehyde; 35 amyl cinnamic aldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; coumarin; decalactone gamma; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid

lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8-hexamethylcyclopenta-gamma-2-benzopyrane; beta-naphthol methyl ether; ambroxane; dodecahydro-3a,6,6,9a-tetramethyl-naphtho[2,1b]furan; cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; 5 tricyclodecenyl propionate; tricyclodecenyl acetate; benzyl salicylate; cedryl acetate; and para-(tert-butyl) cyclohexyl acetate.

Particularly preferred perfume materials are those that provide the largest odor improvements in finished product compositions containing cellulases. These perfumes 10 include but are not limited to: hexyl cinnamic aldehyde; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; benzyl salicylate; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; para-tert-butyl cyclohexyl acetate; methyl dihydro jasmonate; beta-naphthol methyl ether; methyl beta-naphthyl ketone; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; 1,3,4,6,7,8-15 hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gamma-2-benzopyrane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; anisaldehyde; coumarin; cedrol; vanillin; cyclopentadecanolide; tricyclodecenyl acetate; and tricyclodecenyl propionate.

Other perfume materials include essential oils, resinoids, and resins from a variety of 20 sources including, but not limited to: Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander and lavandin. Still other perfume chemicals include phenyl ethyl alcohol, terpineol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)-cyclohexanol acetate, benzyl acetate, and eugenol. Carriers such as diethylphthalate can be used in the finished perfume 25 compositions.

Other Ingredients

A wide variety of other ingredients useful in detergent compositions can be included in 30 the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds 35 boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sulfonates noted above is also advantageous. If desired,

water-soluble magnesium and/or calcium salts such as MgCl₂, MgSO₄, CaCl₂, CaSO₄, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

5 Various detergents ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detergent ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detergent ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detergent function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C13-15 ethoxylated alcohol (EO 7) nonionic surfactant. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for 25 solubilizing surfactant, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

30 The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Liquid dishwashing product formulations preferably have a pH between 6.8 and 9.0. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, 35 alkalis, acids, etc., and are well known to those skilled in the art.

Granules Manufacture

Adding the alkoxylated cationics of this invention into a crutcher mix, followed by conventional spray drying, helps remove any residual, potentially malodorous, short-chain amine contaminants. In the event the formulator wishes to prepare an admixable particle containing the alkoxylated cationics for use in, for example, a high density granular detergent, it is preferred that the particle composition not be highly alkaline. Processes for preparing high density (above 650 g/l) granules are described in U.S. Patent 5,366,652. Such particles may be formulated to have an effective pH in-use of 9, or below, to avoid the odor of impurity amines. This can be achieved by adding a small amount of acidity source such as boric acid, citric acid, or the like, or an appropriate pH buffer, to the particle. In an alternate mode, the prospective problems associated with amine malodors can be masked by use of perfume ingredients, as disclosed herein.

15

Examples

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

In the following examples, the abbreviated component identifications have the following meanings:

25	LAS	:	Sodium linear C ₁₂ alkyl benzene sulfonate
	TAS	:	Sodium tallow alkyl sulfate
	C45AS	:	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate
	C _x yE _z S	:	Sodium C _{1x} -C _{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
30	C45E7	:	A C ₁₄ -15 predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
	C25E3	:	A C ₁₂ -15 branched primary alcohol condensed with an average of 3 moles of ethylene oxide
35	C25E5	:	A C ₁₂ -15 branched primary alcohol condensed with an average of 5 moles of ethylene oxide

	CocoEO2	:	$R_1.N^+(CH_3)(C_2H_4OH)_2$ with $R_1 = C_{12}-C_{14}$
	Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
5	TFAA	:	$C_{16}-C_{18}$ alkyl N-methyl glucamide
	TPKFA	:	$C_{12}-C_{14}$ topped whole cut fatty acids
	STPP	:	Anhydrous sodium tripolyphosphate
	Zeolite A	:	Hydrated Sodium Aluminosilicate of formula $Na_{12}(AlO_2SiO_2)_{12} \cdot 27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers
10	NaSKS-6	:	Crystalline layered silicate of formula $\delta \cdot Na_2Si_2O_5$
	Citric acid	:	Anhydrous citric acid
	Carbonate	:	Anhydrous sodium carbonate with a particle size between 200 μm and 900 μm
15	Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400 μm and 1200 μm
	Silicate	:	Amorphous Sodium Silicate ($SiO_2:Na_2O$; 2.0 ratio)
	Sodium sulfate	:	Anhydrous sodium sulfate
20	Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 μm and 850 μm
	MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight 70,000.
	CMC	:	Sodium carboxymethyl cellulose
25	Protease	:	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
	Alcalase	:	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
	Cellulase	:	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
30			
	Amylase	:	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl
	60T		
35	Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by Lipolase

	Endolase	: Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
	PB4	: Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
5	PB1	: Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
	Percarbonate	: Sodium Percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
10	NOBS	: Nonanoyloxybenzene sulfonate in the form of the sodium salt.
	TAED	: Tetraacetyl ethylenediamine
	DTPMP:	: Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest
	2060	
15	Photoactivated	: Sulfonated Zinc Phthalocyanine encapsulated in bleach dextrin soluble polymer
	Brightener 1	: Disodium 4,4'-bis(2-sulphostyryl)biphenyl
	Brightener 2	: Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
20	HEDP	: 1,1-hydroxyethane diphosphonic acid
	PVNO	: Polyvinylpyridine N-oxide
	PVPVI	: Copolymer of polyvinylpyrrolidone and vinylimidazole
25	SRA 1	: Sulfonylbenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
	SRA 2	: Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
	Silicone antifoam :	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
30		

In the following Examples all levels are quoted as % by weight of the composition.

The following detergent formulations according to the present invention are prepared, where A and C are phosphorus-containing detergent compositions and B is a zeolite-containing detergent composition.

		A	B	C
5	Blown Powder			
	STPP	24.0	-	24.0
	Zeolite A	-	24.0	-
	C45AS	8.0	5.0	11.0
	MA/AA	2.0	4.0	2.0
10	LAS	6.0	8.0	11.0
	TAS	1.5	-	-
	CocoMeEO2*	1.5	1.0	2.0
	Silicate	7.0	3.0	3.0
	CMC	1.0	1.0	0.5
15	Brightener 2	0.2	0.2	0.2
	Soap	1.0	1.0	1.0
	DTPMP	0.4	0.4	0.2
	Spray On			
	C45E7	2.5	2.5	2.0
20	C25E3	2.5	2.5	2.0
	Silicone antifoam	0.3	0.3	0.3
	Perfume	0.3	0.3	0.3
	Dry additives			
	Carbonate	6.0	13.0	15.0
25	PB4	-	4.0	10.0
	PB1	4.0	-	0
	Percarbonate	18.0	18.0	21.0
	TAED	3.0	3.0	-
	Photoactivated bleach	0.02	0.02	0.02
30	Protease	1.0	1.0	1.0
	Lipase	0.4	0.4	0.4
	Amylase	0.25	0.30	0.15
	Dry mixed sodium sulfate	3.0	3.0	5.0
	Balance (Moisture &			
35	Miscellaneous)	To: 100.0	100.0	100.0
	Density (g/litre)	630	670	670

*The AQA-1 (CocoMeEO2) surfactant of the Example may be replaced by an equivalent amount of any of surfactants AQA-2 through AQA-22 or other AQA surfactants herein.

EXAMPLE II

The following detergent formulations, according to the present invention are prepared:

		D	E	F
5	<u>Blown Powder</u>			
	Zeolite A	30.0	22.0	6.0
	Sodium sulfate	19.0	5.0	7.0
	MA/AA	3.0	3.0	6.0
	LAS	13.0	11.0	21.0
10	C45AS	8.0	7.0	7.0
	CocoMeEO2*	1.0	1.0	1.0
	Silicate	-	1.0	5.0
	Soap	-	-	2.0
	Brightener 1	0.2	0.2	0.2
15	Carbonate	8.0	16.0	20.0
	DTPMP	-	0.4	0.4
	<u>Spray On</u>			
	C45E7	1.0	1.0	1.0
	Dry additives			
20	PVPVI/PVNO	0.5	0.5	0.5
	Protease	1.0	1.0	1.0
	Lipase	0.4	0.4	0.4
	Amylase	0.1	0.1	0.1
	Cellulase	0.1	0.1	0.1
25	NOBS	-	6.1	4.5
	Percarbonate	7.0	5.0	6.0
	Sodium sulfate	-	6.0	-
	<u>Balance (Moisture & Miscellaneous)</u>	To: 100	100	100

30 *The AQA-1 (CocoMeEO2) surfactant of the Example may be replaced by an equivalent amount of any of surfactants AQA-2 through AQA-22 or other AQA surfactants herein.

EXAMPLE III

The following high density detergent formulations, according to the present invention are prepared:

		G	H	I
5	Blown Powder			
	Zeolite A	15.0	15.0	15.0
	Sodium sulfate	0.0	5.0	0.0
	LAS	3.0	3.0	3.0
10	CocoMeEO2*	1.0	1.5	1.5
	DTPMP	0.4	0.4	0.4
	CMC	0.4	0.4	0.4
	MA/AA	4.0	2.0	2.0
15	Agglomerates			
	LAS	5.0	5.0	5.0
	TAS	2.0	2.0	1.0
	Silicate	3.0	3.0	4.0
	Zeolite A	8.0	8.0	8.0
	Carbonate	8.0	8.0	4.0
20	Spray On			
	Perfume	0.3	0.3	0.3
	C45E7	2.0	2.0	2.0
	C25E3	2.0	-	-
25	Dry additives			
	Citrate	5.0	-	2.0
	Bicarbonate	-	3.0	-
	Carbonate	8.0	15.0	10.0
	TAED	6.0	2.0	5.0
	Percarbonate	13.0	7.0	10.0
30	Polyethylene oxide of MW 5,000,000	-	-	0.2
	Bentonite clay	-	-	10.0
	Protease	1.0	1.0	1.0
	Lipase	0.4	0.4	0.4
35	Amylase	0.6	0.6	0.6
	Cellulase	0.6	0.6	0.6

		60		
	Silicone antifoam	5.0	5.0	5.0
	Dry additives			
	Sodium sulfate	0.0	3.0	0.0
	Balance (Moisture &			
5	Miscellaneous)	To: 100.0	100.0	100.0
	Density (g/litre)	850	850	850

*The AQA-1 (CocoMeEO2) surfactant of the Example may be replaced by an equivalent amount of any of surfactants AQA-2 through AQA-22 or other AQA surfactants herein.

EXAMPLE IV

The following high density detergent formulations according to the present invention
15 are prepared:

		M	N
	Blown Powder		
	Zeolite A	2.5	2.5
20	Sodium sulfate	1.0	1.0
	CocoMeEO2*	1.5	1.5
	Agglomerate		
	C45AS	11.0	14.0
	Zeolite A	15.0	6.0
25	Carbonate	4.0	8.0
	MA/AA	4.0	2.0
	CMC	0.5	0.5
	DTPMP	0.4	0.4
	Spray On		
30	C25ES	5.0	5.0
	Perfume	0.5	0.5
	Dry Adds		
	HEDP	0.5	0.3
	SKS 6	13.0	10.0
35	Citrate	3.0	1.0
	TAED	5.0	7.0

	Percarbonate	15.0	15.0
	SRA 1	0.3	0.3
	Protease	1.4	1.4
	Lipase	0.4	0.4
5	Cellulase	0.6	0.6
	Amylase	0.6	0.6
	Silicone antifoam	5.0	5.0
	Brightener 1	0.2	0.2
	Brightener 2	0.2	-

10. Balance (Moisture &

Miscellaneous)	To:	100	100
Density (g/litre)		850	850

*The AQA-1 (CocoMeEO₂) surfactant of the Example may be replaced by an equivalent amount of any of surfactants AQA-2 through AQA-22 or other AQA surfactants herein.

Any of the granular detergent compositions provided herein may be tabletted using known tabletting methods to provide detergent tablets.

20 The manufacture of heavy duty liquid detergent compositions, especially those designed for fabric laundering, which comprise a non-aqueous carrier medium can be conducted in the manner disclosed in more detail hereinafter. In an alternate mode, such non-aqueous compositions can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate detergents (e.g., bleaching agents, as disclosed hereinabove) stably suspended therein.

25 Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references. The AQA surfactants are incorporated in the compositions at the levels and in the manner described hereinabove for the manufacture of other laundry detergent compositions.

30

The liquid phase will generally comprise from 35% to 99% by weight of the detergent compositions herein. More preferably, the liquid phase will comprise from 50% to 95% by weight of the compositions. Most preferably, the liquid phase will comprise
5 from 45% to 75% by weight of the compositions herein. The liquid phase of the detergent compositions herein essentially contains relatively high concentrations of a certain type anionic surfactant combined with a certain type of nonaqueous, liquid diluent.

10 (A) Essential Anionic Surfactant

The anionic surfactant is an essential component of the nonaqueous liquid phase and is selected from the alkali metal salts of alkylbenzene sulfonic acids in which the alkyl group contains from 10 to 16 carbon atoms, in straight chain or branched chain configuration. (See U.S. Patents 2,220,099 and 2,477,383, incorporated herein by reference.) Especially preferred are the sodium and potassium linear straight chain alkylbenzene sulfonates (LAS) in which the average number of carbon atoms in the alkyl group is from 11 to 14. Sodium C₁₁-C₁₄ LAS is especially preferred.
15
20 The alkylbenzene sulfonate anionic surfactant will be dissolved in the nonaqueous liquid diluent which makes up the second essential component of the nonaqueous phase. To form the structured liquid phase required for suitable phase stability and acceptable rheology, the alkylbenzene sulfonate anionic surfactant is generally present to the extent of from 30% to 65% by weight of the liquid phase. More preferably, the alkylbenzene sulfonate anionic surfactant will comprise from 35% to 50% by weight of the
25 nonaqueous liquid phase of the compositions herein. Utilization of this anionic surfactant in these concentrations corresponds to an anionic surfactant concentration in the total composition of from 15% to 60% by weight, more preferably from 20% to 40% by weight, of the composition.

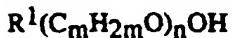
30

(B) Nonaqueous Liquid Diluent

To form the liquid phase of the detergent compositions, the hereinbefore described alkylbenzene sulfonate anionic surfactant is combined with a nonaqueous liquid diluent
35 which contains two essential components. These two components are a liquid alcohol alkoxylate material and a nonaqueous, low-polarity organic solvent.

i) Alcohol Alkoxylates

One essential component of the liquid diluent used to form the compositions herein comprises an alkoxylated fatty alcohol material. Such materials are themselves also 5 nonionic surfactants. Such materials correspond to the general formula:



wherein R^1 is a C₈ - C₁₆ alkyl group, m is from 2 to 4, and n ranges from 2 to 12. Preferably R^1 is an alkyl group, which may be primary or secondary, that contains 10 from 9 to 15 carbon atoms, more preferably from 10 to 14 carbon atoms. Preferably 10 also the alkoxylated fatty alcohols will be ethoxylated materials that contain from 2 to 12 ethylene oxide moieties per molecule, more preferably from 3 to 10 ethylene oxide moieties per molecule.

The alkoxylated fatty alcohol component of the liquid diluent will frequently have a 15 hydrophilic-lipophilic balance (HLB) which ranges from 3 to 17. More preferably, the HLB of this material will range from 6 to 15, most preferably from 8 to 15.

Examples of fatty alcohol alkoxylates useful as one of the essential components of the 20 nonaqueous liquid diluent in the compositions herein will include those which are made from alcohols of 12 to 15 carbon atoms and which contain 7 moles of ethylene oxide. Such materials have been commercially marketed under the trade names Neodol 25-7 and Neodol 23-6.5 by Shell Chemical Company. Other useful Neodols include Neodol 1-5, an ethoxylated fatty alcohol averaging 11 carbon atoms in its alkyl chain with 5 25 moles of ethylene oxide; Neodol 23-9, an ethoxylated primary C₁₂ - C₁₃ alcohol having 9 moles of ethylene oxide and Neodol 91-10, an ethoxylated C₉ - C₁₁ primary 30 alcohol having 10 moles of ethylene oxide. Alcohol ethoxylates of this type have also been marketed by Shell Chemical Company under the Dobanol trademark. Dobanol 91-5 is an ethoxylated C₉-C₁₁ fatty alcohol with an average of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxylated C₁₂-C₁₅ fatty alcohol with an average of 7 moles of ethylene oxide per mole of fatty alcohol.

Other examples of suitable ethoxylated alcohols include Tergitol 15-S-7 and Tergitol 15-S-9 both of which are linear secondary alcohol ethoxylates that have been 35 commercially marketed by Union Carbide Corporation. The former is a mixed ethoxylation product of C₁₁ to C₁₅ linear secondary alkanol with 7 moles of ethylene

oxide and the latter is a similar product but with 9 moles of ethylene oxide being reacted.

Other types of alcohol ethoxylates useful in the present compositions are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14-15 carbon atoms and the number of ethylene oxide groups per mole being 11. Such products have also been commercially marketed by Shell Chemical Company.

The alcohol alkoxylate component which is essentially utilized as part of the liquid diluent in the nonaqueous compositions herein will generally be present to the extent of from 1% to 60% of the liquid phase composition. More preferably, the alcohol alkoxylate component will comprise 5% to 40% of the liquid phase. Most preferably, the essentially utilized alcohol alkoxylate component will comprise from 5% to 30% of the detergent composition liquid phase. Utilization of alcohol alkoxylate in these concentrations in the liquid phase corresponds to an alcohol alkoxylate concentration in the total composition of from 1% to 60% by weight, more preferably from 2% to 40% by weight, and most preferably from 5% to 25% by weight, of the composition.

ii) Nonaqueous Low-Polarity Organic Solvent

A second essential component of the liquid diluent which forms part of the liquid phase of the detergent compositions herein comprises nonaqueous, low-polarity organic solvent(s). The term "solvent" is used herein to connote the non-surface active carrier or diluent portion of the liquid phase of the composition. While some of the essential and/or optional components of the compositions herein may actually dissolve in the "solvent"-containing liquid phase, other components will be present as particulate material dispersed within the "solvent"-containing liquid phase. Thus the term "solvent" is not meant to require that the solvent material be capable of actually dissolving all of the detergent composition components added thereto.

The nonaqueous organic materials which are employed as solvents herein are those which are liquids of low polarity. For purposes of this invention, "low-polarity" liquids are those which have little, if any, tendency to dissolve sodium percarbonate. Thus relatively polar solvents such as ethanol should not be utilized. Suitable types of low-polarity solvents useful in the nonaqueous liquid detergent compositions herein do include non-vicinal C₄-C₈ alkylene glycols, alkylene glycol mono lower alkyl ethers,

lower molecular weight polyethylene glycols, lower molecular weight methyl esters and amides.

A preferred type of nonaqueous, low-polarity solvent for use in the compositions herein

5 comprises the non-vicinal C₄-C₈ branched or straight chain alkylene glycols. Materials of this type include hexylene glycol (4-methyl-2,4-pentanediol), 1,6-hexanediol, 1,3-butylene glycol and 1,4-butylene glycol. Hexylene glycol is the most preferred.

Another preferred type of nonaqueous, low-polarity solvent for use herein comprises

10 the mono-, di-, tri-, or tetra- C₂-C₃ alkylene glycol mono C₂-C₆ alkyl ethers. The specific examples of such compounds include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monoethyl ether, and dipropylene glycol monobutyl ether. Diethylene glycol monobutyl ether and dipropylene glycol monobutyl ether are especially preferred. Compounds of the type

15 have been commercially marketed under the tradenames Dowanol, Carbitol, and Cellosolve.

Another preferred type of nonaqueous, low-polarity organic solvent useful herein

20 comprises the lower molecular weight polyethylene glycols (PEGs). Such materials are those having molecular weights of at least 150. PEGs of molecular weight ranging from 200 to 600 are most preferred.

Yet another preferred type of non-polar, nonaqueous solvent comprises lower molecular weight methyl esters. Such materials are those of the general formula: R¹-C(O)-OCH₃

25 wherein R¹ ranges from 1 to 18. Examples of suitable lower molecular weight methyl esters include methyl acetate, methyl propionate, methyl octanoate, and methyl dodecanoate.

The nonaqueous, low-polarity organic solvent(s) employed should, of course, be

30 compatible and non-reactive with other composition components, e.g., bleach and/or activators, used in the liquid detergent compositions herein. Such a solvent component will generally be utilized in an amount of from 1% to 70% by weight of the liquid phase. More preferably, the nonaqueous, low-polarity organic solvent will comprise from 10% to 60% by weight of the liquid phase, most preferably from 20% to 50% by weight, of the liquid phase of the composition. Utilization of this organic solvent in these concentrations in the liquid phase corresponds to a solvent concentration in the

total composition of from 1% to 50% by weight, more preferably from 5% to 40% by weight, and most preferably from 10% to 30% by weight, of the composition.

iii) Alcohol Alkoxylate To Solvent Ratio

5 The ratio of alcohol alkoxylate to organic solvent within the liquid diluent can be used to vary the rheological properties of the detergent compositions eventually formed. Generally, the weight ratio of alcohol alkoxylate to organic solvent will range from 50:1 to 1:50. More preferably, this ratio will range from 3:1 to 1:3.

iv) Liquid Diluent Concentration

10 As with the concentration of the alkylbenzene sulfonate anionic surfactant mixture, the amount of total liquid diluent in the nonaqueous liquid phase herein will be determined by the type and amounts of other composition components and by the desired composition properties. Generally, the liquid diluent will comprise from 35% to 70% of the nonaqueous liquid phase of the compositions herein. More preferably, the liquid diluent will comprise from 50% to 65% of the nonaqueous liquid phase. This corresponds to a nonaqueous liquid diluent concentration in the total composition of from 15% to 70% by weight, more preferably from 20% to 50% by weight, of the composition.

20 SOLID PHASE

The nonaqueous detergent compositions herein also essentially comprise from 1% to 65% by weight, more preferably from 5% to 50% by weight, of a solid phase of particulate material which is dispersed and suspended within the liquid phase. Generally such particulate material will range in size from 0.1 to 1500 microns. More preferably such material will range in size from 5 to 200 microns.

30 The particulate material utilized herein can comprise one or more types of detergent composition components which in particulate form are substantially insoluble in the nonaqueous liquid phase of the composition. The types of particulate materials which can be utilized are described in detail as follows:

COMPOSITION PREPARATION AND USE

The nonaqueous liquid detergent compositions herein can be prepared by combining the essential and optional components thereof in any convenient order and by mixing, e.g., agitating, the resulting component combination to form the phase stable compositions herein. In a typical process for preparing such compositions, essential and certain

5 preferred optional components will be combined in a particular order and under certain conditions.

In the first step of such a typical preparation process, an admixture of the alkylbenzene sulfonate anionic surfactant and the two essential components of the nonaqueous diluent 10 is formed by heating a combination of these materials to a temperature from 30°C to 100°C.

In a second process step, the heated admixture formed as hereinbefore described is maintained under shear agitation at a temperature from 40°C to 100°C for a period of 15 from 2 minutes to 20 hours. Optionally, a vacuum can be applied to the admixture at this point. This second process step serves to completely dissolve the anionic surfactant in the nonaqueous liquid phase.

In a third process step, this liquid phase combination of materials is cooled to a 20 temperature of from 0°C to 35°C. This cooling step serves to form a structured, surfactant-containing liquid base into which the particulate material of the detergent compositions herein can be added and dispersed.

Particulate material is added in a fourth process step by combining the particulate 25 material with the liquid base which is maintained under conditions of shear agitation. When more than one type of particulate material is to be added, it is preferred that a certain order of addition be observed. For example, while shear agitation is maintained, essentially all of any optional surfactants in solid particulate form can be added in the form of particles ranging in size from 0.2 to 1,000 microns. After addition of any 30 optional surfactant particles, particles of substantially all of an organic builder, e.g., citrate and/or fatty acid, and/or an alkalinity source, e.g., sodium carbonate, can be added while continuing to maintain this admixture of composition components under shear agitation. Other solid form optional ingredients can then be added to the composition at this point. Agitation of the mixture is continued, and if necessary, can 35 be increased at this point to form a uniform dispersion of insoluble solid phase particulates within the liquid phase.

After some or all of the foregoing solid materials have been added to this agitated mixture, the particles of the highly preferred peroxygen bleaching agent can be added to the composition, again while the mixture is maintained under shear agitation. By

5 adding the peroxygen bleaching agent material last, or after all or most of the other components, and especially after alkalinity source particles, have been added, desirable stability benefits for the peroxygen bleach can be realized. If enzyme prills are incorporated, they are preferably added to the nonaqueous liquid matrix last.

10 As a final process step, after addition of all of the particulate material, agitation of the mixture is continued for a period of time sufficient to form compositions having the requisite viscosity and phase stability characteristics. Frequently this will involve agitation for a period of from 1 to 30 minutes.

15 As a variation of the composition preparation procedure hereinbefore described, one or more of the solid components may be added to the agitated mixture as a slurry of particles premixed with a minor portion of one or more of the liquid components. Thus a premix of a small fraction of the alcohol alkoxylate and/or nonaqueous, low-polarity solvent with particles of the organic builder material and/or the particles of the

20 inorganic alkalinity source and/or particles of a bleach activator may be separately formed and added as a slurry to the agitated mixture of composition components. Addition of such slurry premixes should precede addition of peroxygen bleaching agent and/or enzyme particles which may themselves be part of a premix slurry formed in analogous fashion.

25 The compositions of this invention, prepared as hereinbefore described, can be used to form aqueous washing solutions for use in the laundering and bleaching of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous

30 laundering/bleaching solutions. The aqueous washing/bleaching solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered and bleached therewith.

35 An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering/bleaching solutions can comprise amounts sufficient to form from 500 to 7,000 ppm of composition in aqueous solution. More preferably, from 800 to

3,000 ppm of the detergent compositions herein will be provided in aqueous washing/bleaching solution.

EXAMPLE V

5

A non-limiting example of a bleach-containing nonaqueous liquid laundry detergent is prepared having the composition as set forth in Table I.

Table I

	<u>Component</u>	<u>Wt. % Range (% wt.)</u>	
10	<u>Liquid Phase</u>		
	Na C ₁₂ Linear alkylbenzene sulfonate (LAS)	25.3	18-35
	C ₁₂₋₁₄ , EO5 alcohol ethoxylate	13.6	10-20
	Hexylene glycol	27.3	20-30
	Perfume	0.4	0-1.0
15	AQA-1*	2.0	1-3.0
	<u>Solids</u>		
	Protease enzyme	0.4	0-1.0
	Na ₃ Citrate, anhydrous	4.3	3-6
	Sodium percarbonate	3.4	2-7
20	Sodium nonanoyloxybenzene sulfonate (NOBS)	8.0	2-12
	Sodium carbonate	13.9	5-20
	Diethyl triamine pentaacetic acid (DTPA)	0.9	0-1.5
	Brightener	0.4	0-0.6
	Suds Suppressor	0.1	0-0.3
25	Minors	Balance	---

*CocoMeEO2. AQA-1 may be replaced by AQA surfactants 2-22 or other AQA surfactants herein.

30 The composition is prepared by mixing the AQA and LAS, then the hexylene glycol and alcohol ethoxylate, together at 54°C (130°F) for 1/2 hour. This mixture is then cooled to 29°C (85°F) whereupon the remaining components are added. The resulting composition is then stirred at 29°C (85°F) for another 1/2 hour.

35 The resulting composition is a stable anhydrous heavy duty liquid laundry detergent which provides excellent stain and soil removal performance when used in normal fabric laundering operations.

The foregoing Examples illustrate the present invention as it relates to fabric laundering compositions, whereas the following Examples are intended to illustrate other types of cleaning compositions according to this invention, but are not intended to be limiting
5 thereof.

Modern, high performance hand dishwashing compositions can contain ingredients which are designed to provide specific in-use product attributes such as grease cutting ability, high sudsing, mildness and skin feel benefits. Such ingredients for use with the
10 AQA surfactants herein include, for example, amine oxide surfactants, betaine and/or sulfainine surfactants, alkyl sulfate and alkyl ethoxy sulfate surfactants, liquid carriers, especially water and water/propylene glycol mixtures, natural oils such lemon oil. In addition, preferred liquid and/or gel hand dishwashing compositions may also contain calcium ions, magnesium ions, or mixtures of calcium/magnesium ions, which afford
15 additional grease cutting performance advantages especially when used in combination with deterutive mixtures comprising the AQA surfactant herein in combination with, for example, amine oxide, alkyl sulfates and alkyl ethoxy sulfates. Magnesium or calcium or mixed Mg/Ca ion sources typically comprise from 0.01% to 4%, preferably from 0.02% to 2%, by weight, of such compositions. Various water-soluble sources of these
20 ions include, for example, sulfate, chloride and acetate salts. Moreover, these compositions may also contain nonionic surfactants, especially those of the polyhydroxy fatty acid amide and alkyl polyglucaside classes. Preferred are the C₁₂-C₁₄ (coconut alkyl) members of these classes. An especially preferred nonionic surfactant for use in hand dishwashing liquids is C₁₂-C₁₄ N-methylglucamide. Preferred amine oxides
25 include C₁₂-C₁₄ dimethylamine oxide. The alkyl sulfates and alkyl ethoxy sulfates are as described hereinabove. Usage levels for such surfactants in dishwashing liquids is typically in the range from 3% to 50% of the finished composition. The formulation of dishwashing liquid compositions has been described in more detail in various patent publications including U.S. 5,378,409, U.S. 5,376,310 and U.S. 5,417,893,
30 incorporated herein by reference.

Modern automatic dishwashing detergents can contain bleaching agents such as hypochlorite sources; perborate, percarbonate or persulfate bleaches; enzymes such as proteases, lipases and amylases, or mixtures thereof; rinse-aids, especially nonionic surfactants; builders, including zeolite and phosphate builders; low-sudsing deterutive surfactants, especially ethylene oxide/propylene oxide condensates. Such compositions
35

are typically in the form of granules or gels. If used in gel form, various gelling agents known in the literature can be employed. The following Examples A and B further illustrate the invention herein with respect to a granular phosphate-containing automatic dishwashing detergent.

5

EXAMPLE VI

INGREDIENTS	% by weight of active material	
	A	B
10 STPP (anhydrous) ¹	31	26
Sodium Carbonate	22	32
Silicate (% SiO ₂)	9	7
Surfactant (nonionic)	3	1.5
NaDCC Bleach ²	2	-
15 AQA-1*	0.5	1.0
Sodium Percarbonate	3.2	5
TAED	--	1.5
Savinase (Au/g)	0.04	0.04
Termamyl (Amp/g)	425	425
20 Sulfate	25	25
Perfume/Minors	to 100%	to 100%

¹Sodium tripolyphosphate
²Sodium dichlorocyanurate

*The AQA-1 surfactant can be replaced by AQA-2 through AQA-22.

25

Various gelling agents such as CMC, clays, can be used in the compositions to provide varying degrees of viscosity or rigidity, according to the desires of the formulator.

EXAMPLE VII

30 The following hand wash laundry detergent formulations, according to the present invention, are prepared by mixing the ingredients together in the percentage weight amounts as indicated below.

	A	B	C	D
LAS	15.0	12.0	15.0	12.0

TFAA	1.0	2.0	1.0	2.0
C25ES	4.0	2.0	4.0	2.0
AQA-9*	2.0	3.0	3.0	2.0
STPP	25.0	25.0	15.0	15.0
MA/AA	3.0	3.0	3.0	3.0
CMC	0.4	0.4	0.4	0.4
DTPMP	1.0	1.6	1.6	1.6
Carbonate	2.0	2.0	5.0	5.0
Bicarbonate	-	-	2.0	2.0
Silicate	7.0	7.0	7.0	7.0
Protease	1.0	-	1.0	1.0
Amylase	0.4	0.4	0.4	
Lipase	0.12	0.12	-	0.12
Photoactivated bleach	0.3	0.3	0.3	0.3
Sulfate	2.2	2.2	2.2	2.2
PB1	4.0	5.4	4.0	2.3
NOBS	2.6	3.1	2.5	1.7
SRA 1	0.3	0.3	0.7	0.3
Brightener 1	0.15	0.15	0.15	0.15
Balance misc./water	100.0	100.0	100.0	100.0
to 100				

AQA-9*; May be replaced by any AQA surfactant described herein. Preferred AQA surfactants for use in this example are those with from 10 to 15 ethoxy groups; for example AQA-9, AQA-10, AQA-16.

5

EXAMPLE VIII

The following illustrates mixtures of AQA surfactants which can be substituted for the AQA surfactants listed in any of the foregoing Examples. As disclosed hereinabove, such mixtures can be used to provide a spectrum of performance benefits and/or to provide cleaning compositions which are useful over a wide variety of usage conditions. Preferably, the AQA surfactants in such mixtures differ by at least 1.5, preferably 2.5-20, total EO units. Ratio ranges (wt.) for such mixtures are typically 10:1-1:10. Non-limiting examples of such mixtures are as follows.

	<u>Components</u>	<u>Ratio (wt.)</u>
	AQA-1 + AQA-5	1:1
	AQA-1 + AQA-10	1:1
	AQA-1 + AQA-15	1:2
5	AQA-1 + AQA-5 + AQA-20	1:1:1
	AQA-2 + AQA-5	3:1
	AQA-5 + AQA-15	1.5:1
	AQA-1 + AQA-20	1:3

10

Mixtures of the AQA surfactants herein with the corresponding cationic surfactants which contain only a single ethoxylated chain can also be used. Thus, for example, mixtures of ethoxylated cationic surfactants of the formula $R^1N^+CH_3[EO]_x[EO]_yX^-$ and $R^1N^+(CH_3)_2[EO]_zX^-$, wherein R^1 and X are as disclosed above and wherein one of the cationics has $(x+y)$ or z in the range 1-5 preferably 1-2 and the other has $(x+y)$ or z in the range 3-100, preferably 10-20, most preferably 14-16, can be used herein.

15 Such compositions advantageously provide improved detergency performance (especially in a fabric laundering context) over a broader range of water hardness than do the cationic surfactants herein used individually. It has now been discovered that shorter EO cationics (e.g., EO2) improve the cleaning performance of anionic surfactants in soft water, whereas higher EO cationics (e.g., EO15) act to improve hardness tolerance of anionic surfactants, thereby improving the cleaning performance of anionic surfactants in hard water. Conventional wisdom in the detergency art suggests that builders can optimize the performance "window" of anionic surfactants.

20

25 Until now, however, broadening the window to encompass essentially all conditions of water hardness has been impossible to achieve.

The laundry detergent compositions prepared using one or more foregoing combinations of ingredients can optionally be built with any non-phosphate or phosphate builders, or 30 mixtures thereof, typically at levels of from 5% to 70%, by weight of finished composition.

EXAMPLE IX

35 The following illustrates mixtures of conventional non-AQA surfactants which can be used in combination with the AQA surfactants in any of the foregoing Examples, but is

not intended to be limiting thereof. The ratios of non-AQA surfactants in the mixtures are noted in parts by weight of the surfactant mixtures.

Mixtures A-C

5	<u>Ingredients</u>	<u>Ratios</u>
	AS*/LAS	1:1
	AS/LAS	10:1 (pref. 4:1)
	AS/LAS	1:10 (pref. 1:4)

*In the foregoing, the primary, substantially linear AS surfactant can be replaced by an equivalent amount of secondary AS or branched-chain AS, oleyl sulfate, and/or mixtures thereof, including mixtures with linear, primary AS as shown above. The "tallow" chain length AS is particularly useful under hot water conditions, up to the boil. "Coconut" AS is preferred for cooler wash temperatures.

15 The mixtures of alkyl sulfate/anionic surfactants noted above are modified by incorporating a nonionic non-AQA surfactant therein at a weight ratio of anionic (total) to nonionic in the range of 25:1 to 1:5. The nonionic surfactant can comprise any of the conventional classes of ethoxylated alcohols or alkyl phenols, alkylpolyglycosides or polyhydroxy fatty acid amides (less preferred if LAS is present), or mixtures thereof, such as those disclosed hereinabove.

Mixtures D-F

	AS*/AES	1:1
	AS/AES	10:1 (pref. 4:1)
	AS/AES	1:10 (pref. 1:4)

25 *Can be replaced by secondary, branched or oleyl AS as noted above.

The mixtures of AS/AES noted above can be modified by incorporating LAS therein at a weight ratio of AS/AES (total) to LAS in the range from 1:10 to 10:1.

30 The mixtures of AS/AES or their resulting AS/AES/LAS mixtures can also be combined with nonionic surfactants as noted for Mixtures A-C at weight ratios of anionic (total) to nonionic in the range of 25:1 to 1:5.

35 Any of the foregoing mixtures can be modified by the incorporation therein of an amine oxide surfactant, wherein the amine oxide comprises from 1% to 50% of the total surfactant mixture.

Highly preferred combinations of the foregoing non-AQA surfactants will comprise from 3% to 60%, by weight, of the total finished laundry detergent composition. The finished compositions will preferably comprise from 0.25% to 3.5%, by weight, of the
 5 AQA surfactant.

EXAMPLE X

This Example illustrates perfume formulations (A-C) made in accordance with the
 10 invention for incorporation into any of the foregoing Examples of AQA-containing
 detergent compositions. The various ingredients and levels are set forth below.

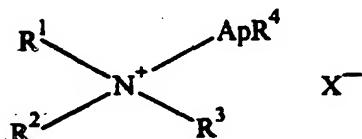
		<u>(% Weight)</u>		
	<u>Perfume Ingredient</u>	<u>A</u>	<u>B</u>	<u>C</u>
	Hexyl cinnamic aldehyde	10.0	-	5.0
15	2-methyl-3-(para-tert-butylphenyl)-propionaldehyde	5.0	5.0	-
	7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene	5.0	10.0	10.0
	Benzyl salicylate	5.0	-	-
	7-acetyl-1,1,3,4,4,6-hexamethyltetralin	10.0	5.0	10.0
20	Para-(tert-butyl) cyclohexyl acetate	5.0	5.0	-
	Methyl dihydro jasmonate	-	5.0	-
	Beta-naphthol methyl ether	-	0.5	-
	Methyl beta-naphthyl ketone	-	0.5	-
	2-methyl-2-(para-iso-propylphenyl)-propionaldehyde	-	2.0	-
25	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gamma-2-benzopyrane	-	9.5	-
	Dodecahydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan	-	-	0.1
	Anisaldehyde	-	-	0.5
30	Coumarin	-	-	5.0
	Cedrol	-	-	0.5
	Vanillin	-	-	5.0
	Cyclopentadecanolide	3.0	-	10.0
	Tricyclodecanyl acetate	-	-	2.0
35	Labdanum resin	-	-	2.0
	Tricyclodecanyl propionate	-	-	2.0

	Phenyl ethyl alcohol	20.0	10.0	27.9
	Terpineol	10.0	5.0	-
	Linalool	10.0	10.0	5.0
	Linalyl acetate	5.0	-	5.0
5	Geraniol	5.0	-	-
	Nerol	-	5.0	-
	2-(1,1-dimethylethyl)-cyclohexanol acetate	5.0	-	-
	Orange oil, cold pressed	-	5.0	-
	Benzyl acetate	2.0	2.0	-
10	Orange terpenes	-	10.0	-
	Eugenol	-	1.0	-
	Diethylphthalate	-	9.5	-
	Lemon oil, cold pressed			10.0
	Total	100.0	100.0	100.0

15 The foregoing perfume compositions are admixed or sprayed onto (typically at levels up to 2% by weight of the total detergent composition) any of the AQA surfactant-containing cleaning (including bleaching) compositions disclosed herein. Improved deposition and/or retention of the perfume or individual components thereof on the surface being cleaned (or bleached) is thus secured.

WHAT IS CLAIMED IS:

1. A composition comprising or prepared by combining, a percarbonate bleach and one or more a non-AQA surfactant and an effective amount of an alkoxylated quaternary ammonium (AOA) cationic surfactant of the formula:



wherein R¹ is a linear, branched or substituted C₈-C₁₈ alkyl, alkenyl, aryl, alkaryl, ether or glycidyl ether moiety, R² is a C₁-C₃ alkyl moiety, R³ and R⁴ can vary independently and are selected from hydrogen, methyl and ethyl, X is an anion, A is C₁-C₄ alkoxy and p is an integer in the range of from 2 to 30.

2. A composition according to Claim 1 which is prepared by mixing the non-AQA surfactant, the AQA surfactant and the percarbonate bleach.

15. 3. A composition according to either of Claims 1 to 2 additionally comprising bleach activator.

4. A composition according to any of Claims 1 to 3 additionally comprising a bleach catalyst.

20

5. A composition according to any of Claims 1 to 4 comprising an additional bleach.

6. A composition according to any of Claims 1 to 5 wherein the non-AQA surfactant is an anionic surfactant.

25

7. A composition according to any of Claims 1 to 6 wherein the ratio of AQA to non-AQA surfactant is from 1:15 to 1:8.

30

8. A composition according to any of Claims 1 to 7 wherein, said AQA surfactant has the formula such that R^1 is C₈-C₁₈ alkyl, R^2 is methyl, A is ethoxy or propoxy groups and p is an integers of from 2 to 8.

9. A composition according to any of Claims 1 to 8 wherein said AQA surfactant has the formula such that R¹ is C₈-C₁₈ alkyl, R² is methyl, A is ethoxy or propoxy groups and p is an integer of from 2 to 4.
- 5 10. A composition according to any of Claims 1 to 9 wherein the formula of the AQA cationic surfactant is such that p is an integer in the range of from 10 to 15.
- 10 11. A composition according to any of Claims 1 to 10 comprising two or more alkoxylated AQA surfactants, or a mixture of a AQA surfactant and a mono-ethoxylated cationic surfactant.
12. A composition according to any of Claims 1 to 11 comprising two or more non-AQA surfactants and a mixture of two or more AQA surfactants.
- 15 13. A composition according to any of Claims 1 to 12 in a granular, bar, aqueous liquid or non-aqueous liquid, or tablet form.
- 20 14. A method for removing soils and stains by contacting said soils and stains with a detergent composition, or aqueous medium comprising said detergent composition, according to any of Claims 1 to 13.
15. A method according to Claim 14 for removing bleach sensitive soil from fabrics.
- 25 16. A method according to either of Claims 14 or 15 which is conducted in an automatic machine.
17. A method according to any of Claims 14 to 16 which is conducted by hand.
- 30 18. A method for enhancing the deposition or substantivity of perfumes or perfume ingredients onto fabrics or other surfaces, comprising contacting said surfaces with a perfume or perfume ingredient in the presence of a AQA surfactant.
19. A method according to Claim 18 which is conducted using a perfume or perfume ingredient in combination with a detergent composition comprising a AQA.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/08439

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C11D3/39 C11D1/65 C11D17/00 //C11D1:62, C11D1:02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8420 Derwent Publications Ltd., London, GB; Class A97, AN 84-123539 XP002044147 & JP 59 059 793 A (LION CORP) , 5 April 1984 see abstract	1,2,6,7, 13
A	EP 0 495 554 A (PROCTER & GAMBLE) 22 July 1992 see page 15 - page 16; claims 1,14-18	1,3,6,7, 13
A	EP 0 002 084 A (PROCTER & GAMBLE) 30 May 1979 cited in the application see claim 1; examples 10-13	1,3,6,7, 13

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "g" document member of the same patent family

1

Date of the actual completion of the international search

21 October 1997

Date of mailing of the international search report

04.11.97

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentstaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
 Fax: (+31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/08439

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 026 529 A (PROCTER & GAMBLE) 8 April 1981 see page 15, line 5 - line 22; claim 1; examples 4,7 -----	1,3,6,7, 13

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 97/08439

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0495554 A	22-07-92	US 5668073 A AU 661672 B AU 1230592 A AU 662736 B AU 1542092 A BR 9205427 A BR 9205428 A BR 9205451 A CA 2099508 A CA 2100097 A CA 2100554 A CN 1064309 A,B CZ 9301410 A EP 0495257 A EP 0495258 A EP 0646165 A HU 65221 A,B JP 6504311 T JP 6505049 T JP 6509122 T MX 9200171 A MX 9200198 A NZ 241308 A SK 72493 A US 5520838 A US 5443750 A WO 9213054 A WO 9213053 A WO 9213057 A	16-09-97 03-08-95 27-08-92 14-09-95 27-08-92 15-03-94 05-04-94 15-03-94 17-07-92 17-07-92 17-07-92 09-09-92 16-03-94 22-07-92 22-07-92 05-04-95 02-05-94 19-05-94 09-06-94 13-10-94 01-05-93 29-01-93 26-07-94 12-01-94 28-05-96 22-08-95 06-08-92 06-08-92 06-08-92
EP 0002084 A	30-05-79	AT 377283 B BE 40 T BR 7807523 A CA 1102202 A CH 644394 A DE 2857300 A FR 2436179 A GB 2040990 A,B JP 54108814 A NL 7815052 A	25-02-85 11-01-80 24-07-79 02-06-81 31-07-84 26-06-80 11-04-80 03-09-80 25-08-79 31-01-80

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 97/08439

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0002084 A		NL 7815052 T US 4347168 A	31-01-80 31-08-82
EP 0026529 A	08-04-81	NONE	